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FACTORS AFFECTING ZINC DISSOLUTION FROM STAINLESS STEEL PRODUCTION DUSTS USING ALKALINE MEDIA

Thesis for the degree of Licentiate of Science in Technology submitted for inspection, Espoo, 27 November, 2014.

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Abstract of Licentiate Thesis

Author

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Title of Thesis

Factors affecting zinc dissolution from stainless steel production dusts using alkaline media

Abstract

Stainless steel production generates significant quantities of flue dusts that are considered as hazardous waste and are normally treated with pyrometallurgical methods in separate treatment plants. These dusts also contain valuable metals but the extraction and recovery of the valuables is difficult due their complex composition. Especially zinc content of the dust causes troubles in treating the dusts.

In this thesis a hydrometallurgical method based on NaOH leaching was investigated as considered to be suitable for on-site treatment. The aim was to selectively remove zinc so that the remaining (Ni, Cr, Fe) oxide material could be recycled back to melting. The studied dust samples included argon-oxygen decarburization (AOD1 and AOD2) converter dusts and electric arc furnace (EAF1 and EAF2) dusts from the two production lines of Outokumpu Stainless Tornio Works.

The effect of five different leaching factors (NaOH concentration, temperature, liquid-to-solid ratio, oxygen/nitrogen gas bubbling and agitation) on zinc dissolution was investigated using fractional factorial designs of the experiments. NaOH concentration, temperature and agitation affected zinc extraction predominantly and the greatest zinc extraction was achieved with high level of those three factors. The maximum amount of extracted zinc was: 80 % from AOD1, 50 % from AOD2, 60 % for EAF1 and 30 % for EAF2. Difference in zinc extraction between the dusts arose from the mineralogical differences. In all dusts zinc occurred both as easily soluble zinc oxide and as poorly-soluble ferrite form.

This study showed that alkaline leaching of zinc from stainless steel AOD and EAF dusts using NaOH solutions is selective and practically no iron, chromium and nickel were dissolved. However, the dissolution of zinc is limited due to the presence of zinc ferrites. The leaching process can work in zinc removal if zinc ferrites are decomposed prior to leaching, for example by roasting.

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Tiivistelmä

Ruostumattoman teräksen valmistuksessa muodostuu huomattavia määriä suodinpölyjä, jotka on luokiteltu haitalliseksi jätteeksi ja käsitellään normaalisti pyrometallurgisin menetelmin erillisissä laitoksissa. Nämä pölyt sisältävät myös arvokkaita metalleja mutta niiden erottaminen ja talteenotto on hankalaa johtuen pölyjen kompleksisesta koostumuksesta. Etenkin pölyn sisältämä sinkki aiheuttaa ongelmia pölyjen käsittelyssä.

Tässä työssä tutkittiin NaOH liuotukseen perustuvaa hydrometallurgista menetelmää, jota pidetään mahdollisena tehtaan yhteydessä toimivaksi. Tarkoitus oli selektiivisesti poistaa sinkki pölyistä niin, että jäljelle jäävä (Ni, Cr, Fe) – oksidimateriaali voitaisiin kierrättää takaisin uuniin. Työssä tutkittiin argon-oxygen decarburization – konvertteri pölyjä (AOD1 ja AOD2) sekä valokaariuunin pölyjä (EAF1 ja EAF2) kahdelta eri tuotantolinjalta Outokummun Tornion tehtailta.

Faktorikoesarjoilla tutkittiin viiden eri liuosmuuttujan (NaOH konsentraatio, lämpötila, neste-kiinteä suhde, happi/typpikuplitus ja sekoitus) vaikutusta sinkin liukenemiseen. Sinkin liukenemiseen vaikuttivat etupäässä NaOH konsentraatio, lämpötila sekä sekoitus ja sinkin liukeneminen oli suurinta näiden kolmen tekijän korkeilla arvoilla. Maksimissaan sinkkiä liukeni n. 80 % AOD1 pölystä, n. 50 % AOD2 pölystä, n. 60 % EAF1 pölystä ja n. 30 % EAF2 pölystä. Eroavuudet sinkin liukenemisprosenteissa johtuivat pölyjen mineralogisen koostumuksen eroavuudesta. Kaikissa pölyissä sinkin todettiin esiintyvän helposti liukenevana sinkkioksidina sekä lähes liukenemattomana sinkkiferriittinä.

Tämä työ osoitti, että sinkki voidaan selektiivisesti liuottaa ruostumattoman teräksen pölyistä NaOH -liuotuksella ja rauta, kromi ja nikkeli eivät käytännössä liuenneet lainkaan. Kuitenkin sinkin ferriittimuoto rajoittaa sen liukenemista mutta emäsliuotusprosessi voisi toimia sinkin poistamiseen ja pölyjen kierrättämiseen mikäli sinkkiferriitit hajotetaan, esimerkiksi pasuttamalla, ennen liuotusta.

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PREFACE

This thesis was carried out in Aalto University's Research Group of Corrosion and Hydrometallurgy from during the years 2009 – 2014. The thesis was part of the METDUST project in the ELEMET research program funded by the Finnish Metals and Engineering Competence Cluster (Fimecc Oy). The financial support of TEKES, Outokumpu Stainless Oyj and Outotec Oyj is gratefully acknowledged.

I wish to express my gratitude to my supervising Professor Olof Forsén and thesis advisor Docent Jari Aromaa for giving me opportunity to work among interesting subjects in the laboratory. I want to thank them for all the help and comments regarding my scientific work. Professor Tomas Havlik from Technical University of Kosice and M.Sc. Hannu Makkonen from Oulu University I want to thank for the analytical work in characterizing the composition of studied dusts used in this thesis. Mr. Terrence Russell deserves the very special thanks for the guidance in planning the experimental set-up and in the analysis of the results.

I thank all the current and former personnel in the laboratory for their help and expertise, and for the all the research and non-research related discussions. Especially thanks to Miia-Maria Pesonen who did her Master's thesis within this project and to Suvi Rantanen who, besides being my friend, also assisted me with experimental work during one summer. The special thanks to Lotta Rintala for being my roommate and problem sharer during this work.

I warmly thank all my friends for giving me other things to think about besides work. Having you around helps me to keep my sense. The Suntio and Stefanov families are warmly thanked for the invaluable support and just being there for me. I thank most lovingly my husband Boris, not only for helping me with some artwork, but most of all, for your love and endless support over the years.

Finally, the very special thank belongs to my greatest precious, Maksim, for being the most wonderful creature in the world and inspiration of my life. Maksim and Boris, you two are the true meaning for living!

Espoo, November 2014

Anna Stefanova

LIST OF PUBLICATIONS

This thesis consists of a compendium and of the following publications, which are referred to in the text by Roman numerals.

I **Anna Stefanova,** Miia Pesonen, Jari Aromaa, Olof Forsén, *Effect of Leaching Parameters on Zinc Removal from Stainless Steel Dusts,* Proceedings of European Metallurgical Conference, Düsseldorf, Germany 2011, pp. 519-532

II **Anna Stefanova**, Jari Aromaa, Olof Forsén, *Alkaline leaching of stainless steel production dust*. Kammel's Quo Vadis Hydrometallurgy 6, Herlany- Kosice, Slovakia, 2012, pp. 208-215.

III **Anna Stefanova,** Jari Aromaa, Olof Forsén, *Alkaline leaching of zinc from argon oxygen decarburization dust from stainless steel production.* Physicochemical Problems of Mineral Processing 49(2013) 1. pp. 37-46.

IV **Anna Stefanova,** Jari Aromaa, Olof Forsén, *Alkaline leaching of zinc from stainless steel electric arc furnace dusts.* Physicochemical Problems of Mineral Processing, 51(2015) 1, pp. 293-302. (Accepted 8.8.2014)

AUTHOR'S CONTRIBUTION

Publication I:

A literature part was done by the author and Miia-Maria Pesonen. The experimental set-up was planned and results were analyzed with co-authors. The author wrote the manuscript based on the input from the co-authors.

Publication II, III and IV:

A literature part was done by the author. The experimental work was carried out by author together with co-authors. The author, taking into account the comments of the co-authors, interpreted the results and wrote the manuscript.

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1 INTRODUCTION

Recycling of steel scrap has obvious economic and resource conservational benefits. However, steel industry generates every day significant quantities of dust and the use of scrap as raw material brings harmful elements into furnaces and they end up into dust. In most industrial countries flue dusts from steel production are classified as hazardous waste and must be treated before disposal. On the other hand, these dusts contain valuable metals and they are often treated as a source of raw materials in metal production.

The pressure to reduce pollutants has increased more interest for further utilizing of dusts as secondary raw material [1]. On the other hand, increased use of recycled steel has increased levels of harmful elements. For example, the increased use of galvanized steel has increased the zinc content in the steel making dusts. The recovery of zinc from the dust would save natural resources and eliminate environmental problems. In addition, production of metals from the secondary waste materials, such as steelmaking dusts, consumes less energy. The energy savings in producing zinc from flue dusts can be about 30 % compared to manufacturing from primary sources [2]. Today, around 40 % of worldwide zinc production is composed of recycled or secondary zinc resources [3]. Steel industry filter dusts represented (in 1998) about 6 % of the sources of zinc recycling [4].

Nowadays still about 60 % of dust is used as landfill that mean even 800 000 DMT (dry metric ton) loss of zinc per annum from EAF processes [5]. The profitability of the process for recovering zinc will be highly dependent on the zinc content of the waste and on the market value of the recovered zinc [2]. Other important factors are the cost of landfilling or other disposal and the sufficiency of raw materials from ores. In case of dust treating processes, the economically viable process can be achieved if the operating costs for the process are less than the costs for dumping it. [6]

1.1 Dust formation in stainless steel production

The dust treatment and recycling was studied using Outokumpu Stainless Oy Tornio Works as example case. The stainless steel process chain begins in chrome mine and goes through a ferrochrome and a steel plant until the rolling processes. In ferrochrome treatment silicon and part of carbon is removed with oxygen blowing in a chrome converter. In steel plant stainless steel is typically produced by melting steel scrap with molten or lump ferrochrome and slag formers in an electric arc furnace (EAF) after which chromium-containing steel melt is refined in an argon oxygen decarburization (AOD) converter. From the converter the melt is moved with ladles in which the final composition of steel is set. Outokumpu Stainless Oy and Outokumpu Chrome Oy form one of the largest stainless steel mills in the world and also the world's most integrated single-site operation. The integrated production process begins in an underground chromite mine nearby (in Kemi) and continues in ferrochrome smelter in Tornio where ferrochrome is transferred to two stainless steel melt shops, and further to a rolling mill (Figure 1). [7]

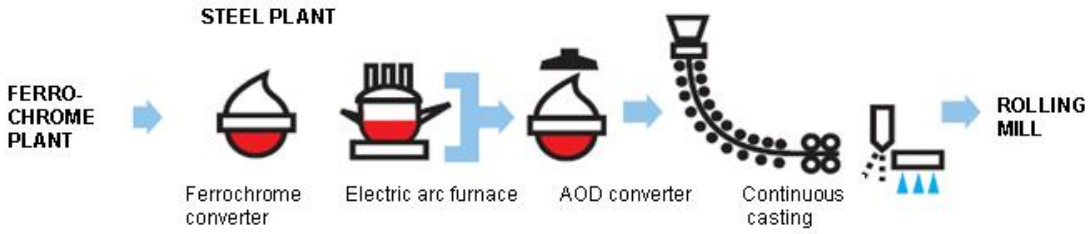


Figure 1. Stainless steel production chain from ferrochrome plant to rolling mill [7].

Stainless steel production generates significant quantities various solid wastes in furnaces and converters, such as in EAF and AOD converter. Emissions and fumes from these are cooled and particulate matter is collected by bag house filters (Figure 2) [8]. During the stainless steel production from 30 to 70 kg of dust and fine waste is generated per ton of steel [9]. In EAF five different sources for dust emission have been identified (Figure 3):

1) volatilization,
2) projection of droplets on the steel bath,
3) projection of fine droplets by bursting of CO bubbles,

4) bursting of droplets in contact with oxidizing atmosphere within surface and

5) direct fly-off of fine solid particles.

The major sources of dust emission are bursting of CO bubbles and volatilization. Around 60 % of dust is formed via bursting of CO bubbles and 27 % via volatilization. The formed dust is very fine-grained and the size of individual dust particles is mostly less than 20 μm. [10]

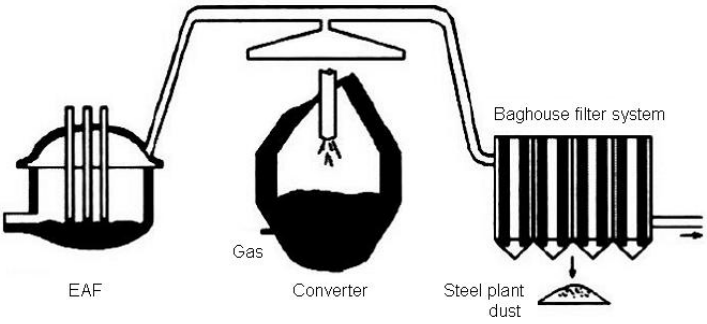


Figure 2. Schematic diagram of dust treatment system in stainless steel plant [8].

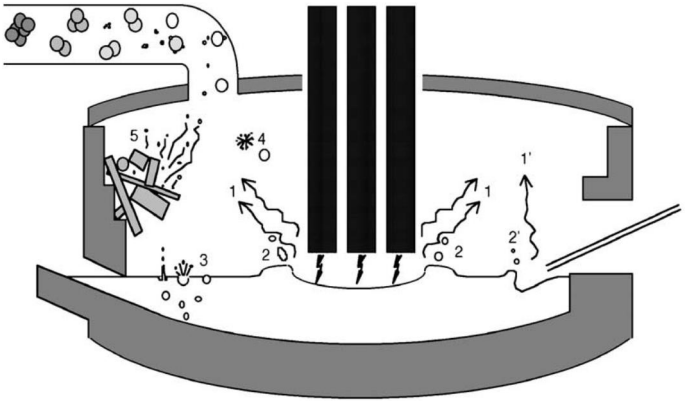


Figure 3. Mechanisms of dust formation in EAF [10].

Dusts from stainless steel production usually contain considerable amounts of valuable metals, such as alloying elements like chromium, nickel and molybdenum and also zinc from recycling of galvanized scrap. The temperature in furnace can reach ≥ 1600 °C and some metals are volatilized and enter to the dust when vapor is cooled and collected [11]. Stainless steel dust consists mainly of oxide phases that are rich in Fe, Cr, Ca, Zn, Mg, Mn and Ni, with minor amounts of phases that contain alkaline metals (K, Na), halogens

(Cl, F), Si, Mo, Pb and S [12]. The chemical compositions of, and crystalline phases present in the dusts vary considerably depending on the steel grade produced, raw materials used, operation conditions and procedures. [13]

In addition to valuable metals, stainless steel flue dusts contain environmentally harmful elements and are thus classified as hazardous waste K061 by US Environmental Protection Agency (EPA) and 10 02 07* by European Waste Code system (EWC) [14, 15]. The disposal or possible reuse of these dusts has been a serious concern for the industry. Because these dusts contain harmful elements such as heavy metals that could dissolve to ground water when stockpiled or landfilled it is necessary to treat them in order to eliminate the harmful compounds [8, 12, 16]. The requirement of treatment makes the disposal of dusts expensive. In addition, production of metals from ores usually consumes more energy than production from waste/secondary materials. From economic and environmental point of view it is desirable to recover the valuables and utilize these wastes [17].

Technologies for treating the steelmaking dusts can be divided into three categories: direct recycling, recovery processes for the valuables and stabilization or vitrification processes [8, 12, 13, 16, 18-22]. Options like stabilization or vitrification aim to placing the dust safely on the dump but then the valuable metals are not recovered and thus lost. However, the direct recycling of dust back to stainless steel production is not possible because it contains considerable amounts of elements that cause operational difficulties in the steel making process. The most problematic element is zinc, which vaporizes easily and condenses to production fumes. Zinc content in stainless steel dusts varies strongly and it is in the range of 1.0 – 16.4 wt% [23-26].

Various pyrometallurgical, hydrometallurgical and combined processes have been developed for treating the steel mill flue dusts in order to recover the valuables and to produce a residue that could be recycled further (Figure 4) [11, 13, 27-30]. Only few of the developed processes have reached commercialization. Today the dust treatment processes are predominantly pyrometallurgical and dusts are recycled in separate treatment plants. There are some plants in commercial operation for processing EAF dusts in the USA, Sweden, Germany and Japan [1]. The oldest and most often applied technology for the recycling of dusty steel mill residues world-wide is the Waelz process

[31]. The Waelz kiln processing is the dominant technology for EAF dust treatment and represents around 80 % of the global capacity [5].

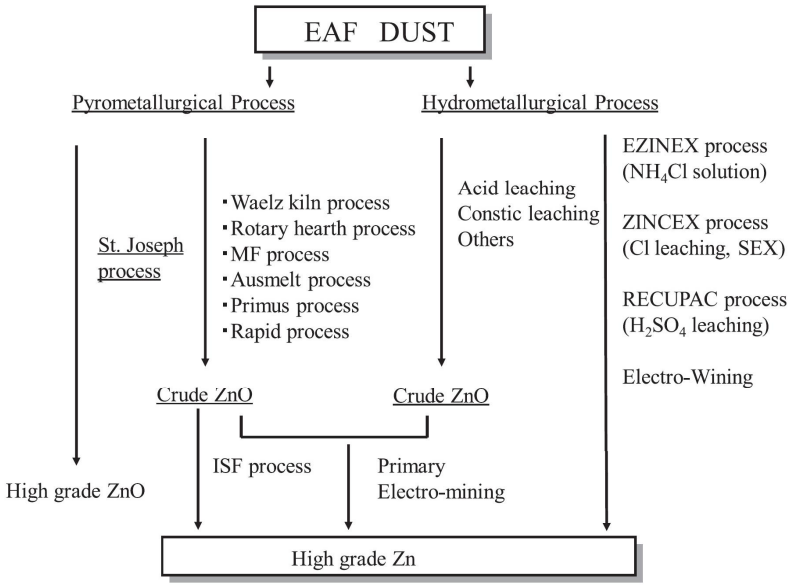


Figure 4. Pyro- and hydrometallurgical treatment processes or EAF dust including the commercial operation processes and the pilot plant operation processes [30]. The processes at laboratory scale and under developing are not listed.

The main purpose of treating stainless steel flue dust is to remove and recover zinc so that iron and alloying element, such as chromium and nickel, containing material/residue can be recycled back to furnaces. Metal extraction from the dusts is difficult due to their complex composition and there are still problems associated with treating this material. The developed processes have not been entirely satisfying [29]. Pyrometallurgical processes perform well when a huge amount of dust is treated at one time but therefore the treatment plants may have a distant location from the steel factory. The transportation of quantities of dust, which is hazardous waste, is expensive and risky. In addition, the drawbacks with pyrometallurgical processes are high consumption of energy, a need of a dust collection system, and generation of worthless residues [27, 32]. Plasma processing of stainless steel dust can recover much of the valuable alloying elements. However, most of the pyrometallurgical processes usually produce only crude zinc oxide (ZnO) with low commercial value and to produce metallic zinc further treatments are needed. [32, 33]

Currently, the dusts from Outokumpu Tornio stainless steel plant are treated with so called Scandust method in the south of Sweden. Scandust uses plasma generators where the dried mixture of dust and sand is charged and smelt to form metal, slag and gases. Metal is cast into granules that are returned to the steelworks and the separated slag can be used for road building or landfilling. The gas cleaning operation produces zinc-rich sludge that is removed for further treatment in an external process. [34]

The driving force for developing hydrometallurgical processes is that they can fit on small scale and thus are considered to be suitable for an on-site treatment [30]. An on-site process is desired to reduce the treatment and transportation cost of the dust [30]. Hydrometallurgical processes are compact and easy to make a closed system [27, 33] when the control of the hazardous elements present in the dust is in better hands. The individual particles in the dust are mostly less than 10 µm and difficult to handle dry, if no previous agglomeration is used [19]. In addition, the reaction kinetics involving this dust should be fast, which suggests that leaching may be an attractive route to treat this kind of material [19, 24].

1.2 Hydrometallurgical processing of flue dusts

The common stages in a hydrometallurgical process are shown in Figure 5. In hydrometallurgical processes, metals are extracted by a leaching stage and then recovered in metallic form by electrolysis or other reduction methods [1]. Depending on a character and composition of the raw material, a suitable solution can be chosen to dissolve the desired metals leaving the gangue in the solid residue.

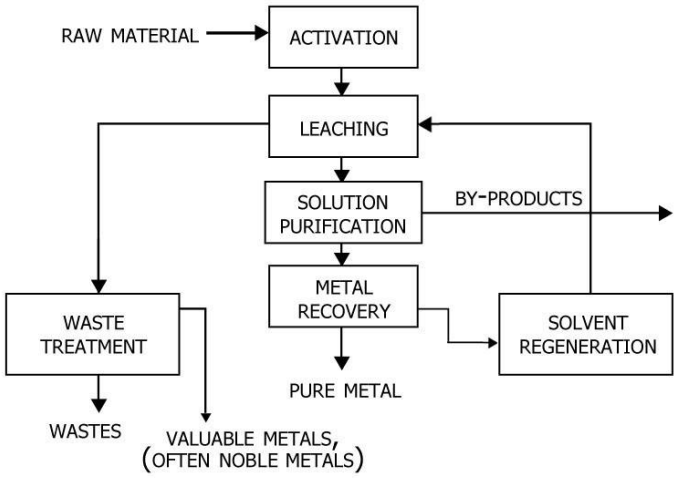


Figure 5. The common stages in a hydrometallurgical process.

The aim of hydrometallurgical treating of steelmaking dusts is to recover the valuable elements contained in the dust and to obtain a non-hazardous residue that can be stored without problem or can be recycled back into steelmaking furnaces. Usually, the most important stage is the leaching stage in which selective solubility of zinc relative to iron compound is critical. Iron in dust is mostly prevalent in Fe_3O_4 phase, 50-80% of zinc is present as ZnO, rest balanced mainly as compound with Fe in a mixed zinc-iron ferrites spinel [24]. Type and concentration of the leaching agent is dependent on chemical composition of source material and mineral from which the metal has to be extracted [4]. Sulfuric acid, hydrochloric acid, ammonia, ammonium carbonate, ammonium chloride, sodium hydroxide, carboxyl acid etc. have been used for the dissolving of zinc and different processes have been developed with planning stage, pilot plant and commercial levels [27]. All of these processes have been developed to remove and recover zinc from EAF dust of unalloyed steel production. No hydrometallurgical process schemes have been documented in the literature for stainless steel dusts that contain valuable alloying elements.

Principally, the two most used leaching methods for treating carbon steel dusts are sulfuric acid (H_2SO_4) and caustic soda (NaOH) leaching. The major advantage with acid solutions is that they are very familiar and low-cost. With sulfuric acid solutions the traditional electrowinning is applicable to obtain metallic zinc [30]. But the main problem with acids is that also iron dissolves. The solution purification process is

difficult and complex when iron is dissolved to leach solution. In addition, the high alkalinity of many dusts consumes a lot of acid for pH adjustment [1, 16]. Among the hydrometallurgical processes the major advantage of alkaline leaching is selectiveness in leaching zinc compared to iron compounds. Thus a relatively clean and iron-free pregnant solution can be achieved and complicated iron removal process is avoided.

So far, the major obstruction in the hydrometallurgical extraction of zinc has been the presence of zinc ferrite ($ZnFe_2O_4$) in the dust, which is insoluble in many solutions [18]. The leaching process should produce an iron-bearing residue with maximum of 0.4 – 1 wt-% zinc in order to recycle it into the steel plant furnaces [27, 35]. For breaking the zinc ferrite structure, pyrometallurgical processes such as roasting, can be used prior to leaching. By low temperature caustic roasting followed by alkaline NaOH leaching zinc ferrites can be decomposed and leaching of zinc could be improved [11, 29]. A process based on alkaline pretreatment and alkaline leaching thus offers an interesting alternative for zinc recycling from stainless steel dusts.

1.3 Target of the study

Dusts from stainless steel production contain many elements making metal extraction complex and difficult. In addition, each dust is unique which makes finding a suitable treatment process even more complicated. Previous studies on hydrometallurgical methods have concentrated on the leaching of carbon steel dusts (mainly from the EAF dust), and for this purpose both acid and alkaline leaching based laboratory and pilot set-ups have been constructed. Only few studies of acidic leaching the dusts from stainless steel production are published [17, 36].

The most important stage in treating the stainless steel production dust is the removal of zinc from the dust. The main problem with zinc is that it hinders the direct recycling of dust back into stainless steel making furnaces. Besides flue dusts can not be reused in zinc smelters as the zinc content is too low for that and they contain high amounts of impurities. In order to recycling dust back into steel making furnaces, the zinc content in the dust should be lowered to as low as 0.1 %. Earlier studies of alkaline leaching of

dusts from iron and steel mills have showed good selectivity in dissolving zinc compared to iron compounds [1, 19, 28].

This study is part of METDUST project in the ELEMET research program funded by the Finnish Metals and Engineering Competence Cluster (Fimecc Oy). The aim of the METDUST project is to develop new processes and technologies for stainless steel mill dust treatment in order to move towards zero-waste plants. The purposes for processing of dusts are recovering the valuable metals in suitable form for use as secondary raw material and capturing of the other economically uninteresting but environmentally critical elements. For the purpose of recycling the stainless steel dusts the iron and valuable alloying elements chromium, nickel and molybdenum should remain in the residue. The elements that are not wanted in the melting of steel charge, like zinc, lead and cadmium, should report into the leach solution for later recovery.

The focus of this study has been on alkaline leaching of two different types of dust from stainless steel production, argon oxygen decarburization (AOD) dust and electric arc furnace (EAF) dust. The main objectives of the study were:

i) To investigate if zinc can be selectively leached out from stainless steel flue dust by alkaline leaching with caustic soda (NaOH).

ii) To determine the main factors that affect the zinc dissolution from stainless steel flue dusts using alkaline (NaOH) leaching. The studied leaching factors were NaOH concentration, temperature, liquid to solid ratio (L/S), redox potential and stirring rate.

iii) To find the possible interactions between the leaching factors.

The target is to selectively leach zinc out of stainless steel making dusts as fast and as much as possible. If zinc can be leached out from stainless steel making dust it would provide an opportunity to effectively recycle the dust back to steel making process and to recover zinc from the dust. A simplified flowsheet of the caustic soda leaching process proposed in this study for treating the dusts from stainless steel production is illustrated in Figure 6.

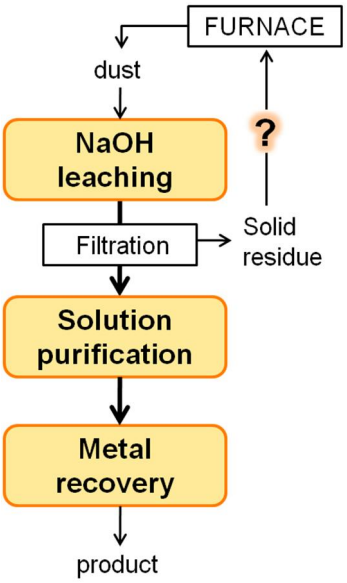


Figure 6. A principal flowsheet of alkaline leaching process for treating the dust from stainless steel production [II].

2 ALKALINE LEACHING

Alkaline leaching offers a method for separation of zinc and lead from the oxidized zinc ores and waste materials. Because very few other elements are leached the consumption of leaching agent is low and a solution containing zinc (and lead) as main element(s) is obtained [22]. Sodium hydroxide is one of the common bases used for leaching amphoteric hydroxides or oxides [37].

2.1 Principles of NaOH leaching

The major advantage of alkaline leaching is the selective solubility of zinc compared to iron compounds that is illustrated in equilibrium diagrams (Figure 7 and Figure 8). The diagrams show that speciation and dissolution of iron hydroxide and zinc oxides are dependent on pH. These diagrams indicate that zinc can be dissolved in either acidic or alkaline media, whereas iron is more readily soluble in acidic media [19].

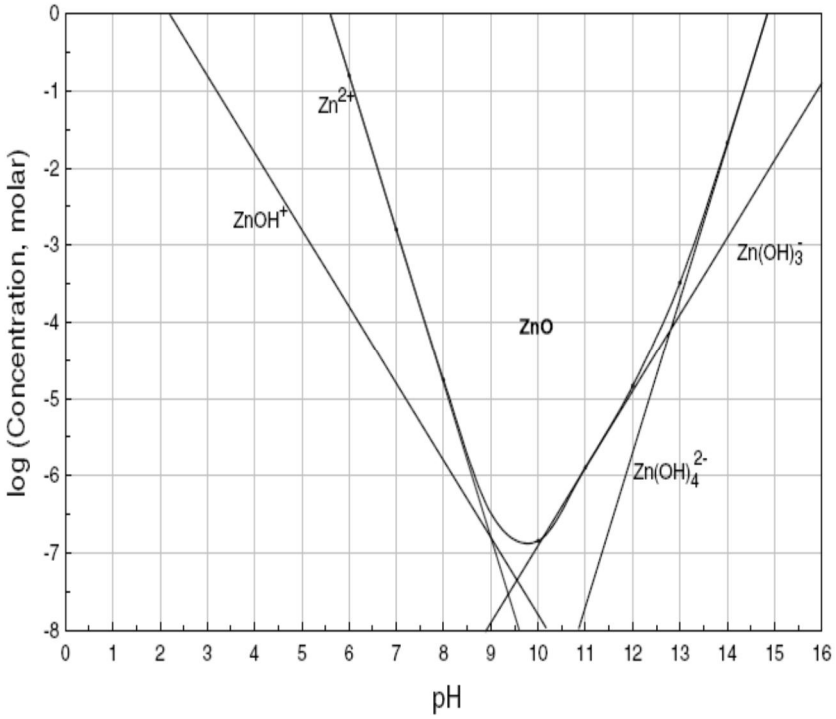
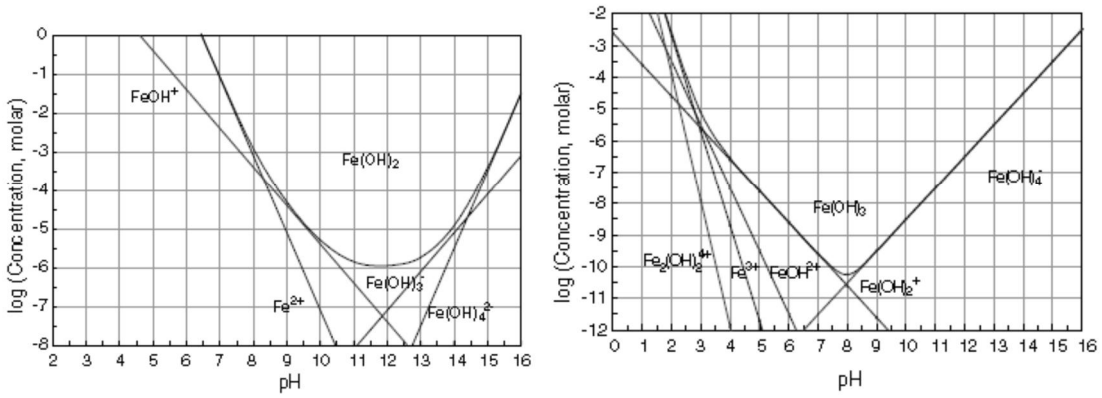


Figure 7. Solubility of ZnO as a function of pH, at 25 °C [19].



a) b)

Figure 8. Solubility of ferrous (a) and ferric (b) hydroxides as a function of pH, at 25 °C [19].

Dusts from stainless steel production contain mainly oxide phases of various metals. Oxides of zinc and lead dissolve easily in alkalis and the main leaching reactions (1) and (2) in strong NaOH solution can be expressed as follows [38]:

$$ZnO(s) + 2NaOH(aq) \rightarrow 2Na^{+}(aq) + (ZnO_2)^{2-}(aq) \quad (1)$$

$$PbO(s) + 2NaOH(aq) \rightarrow 2Na^{+}(aq) + (PbO_2)^{2-}(aq) \quad (2)$$

The other form of zinc, which is present in the dust, is zinc ferrite ($ZnFe_2O_4$). Zinc ferrite is a very stable compound and only partial amount will dissolve in alkalis. If dust contains aluminum hydroxide or silica they can dissolve in alkaline solutions according to reactions (3) and (4) [4]. However, aluminum and silica have found to dissolve relatively little from EAF dust [39].

$$SiO_2(s) + 2NaOH(aq) \rightarrow 2Na^{+}(aq) + (SiO_3)^{2-}(aq) \quad (3)$$

$$Al(OH)_3(s) + NaOH(aq) \rightarrow Na^{+}(aq) + Al(OH)_4^{-}(aq) \quad (4)$$

After NaOH leaching the solids are separated from the leachate. The earlier experiments have shown that the solubility of the certain amphoteric elements in strong alkaline solution decreases in the following sequence Zn > Pb > Al > Cr(III) > Cu [11]. The solubility of Cr(III), Cu and Cd are found to be negligible in the presence of zinc and lead. Also the solubility of lead is decreased if the zinc content in caustic solution is relatively high. Fe, Cd, Ca and Mg have found to remain in the leaching residue [11]. The solid residue that is depleted in zinc and enriched in iron and chromium may be

suitable for recycling back into furnaces in stainless steel production. The leachate contains zinc as predominant element and it can be recovered after solution purification by electrolysis or precipitated as its pure compound.

2.2 Effect of leaching parameters

The most important parameters controlling the efficiency of the leaching process are oxidation potential, concentration of leaching agent, temperature, and pH [4]. Also other factors, such as particle size, agitation and pulp density, are affecting the efficiency of leaching process as having influence on leaching rate. The leaching rate can be increased by [37]:

1. Decreasing particle size.
2. Increasing the speed of agitation, if the leaching process is diffusion controlled (Diffusion-controlled reactions occur so quickly that the formation of products from the activated complex is much faster than the diffusion of reactants).
3. Increasing temperature (less significant for diffusion-controlled).
4. Increasing concentration of the leaching agent (optimum level to maximize selectivity).
5. Decreasing pulp density (small volume of solids).

If an insoluble reaction product is formed on the particles during leaching, the dissolution rate depends on the nature of this product [37]. Based on literature, the main factors affecting on zinc dissolution from steelmaking dust using NaOH solution are described below.

2.2.1 NaOH concentration and temperature

Generally the increase of NaOH concentration increases dissolution of zinc from the dust. However, when the concentration has reached 5 M NaOH, a further increase had only little effect on the leaching (Figure 9) [11]. The concentration of leaching agent should set up to optimum level in order to maximize the selectivity [37]. A phase weight ratio of 3 for NaOH/dust was considered to be sufficient to reach maximum leaching and extraction of zinc [11]. In several experiments NaOH concentrations around 6 M gave zinc recoveries above 65 %, but to reach recoveries of this level also elevated

temperature is needed [1, 19, 33]. The increase of temperature has seen to improve the solubility of zinc in caustic soda leaching of EAF dust [1, 28, 40].

Usually, the dissolution of zinc has been discovered to be very fast, tending to maximum constant value of extraction. The value is, however, seen to be dependent on concentration and temperature at longer leaching times (Figure 10). The additional extraction obtained after 2 hours is most likely due to dissolution of some entrapped zinc or the destruction of zinc ferrites [19]. Nevertheless, in 10 minutes more than 50 % of zinc can be dissolved and 30 – 90 minutes leaching times are reported to be reasonable for higher temperatures [1, 19, 28, 40]. With concentrations 1 – 4 M NaOH temperature has had a significant impact to the leaching time. At 32 °C leaching was found to be complete in 120 minutes, at 95 °C in 30 minutes [40].

Also, it must be taken into consideration that the viscosity of NaOH solutions changes with concentration and temperature (Figure 11) [41] and a change in viscosity has consequences for the diffusion rate of ions and thus for the dissolution of zinc [11]. At temperature of 70 °C the zinc extraction was seen to increase with increased NaOH concentration up to 10 M, but to drop at 12 M, due to increased viscosity [28]. At 60 °C the dissolution of zinc was seen to decrease already in concentrations over 2.5 M NaOH [40]. There seems to be a tendency that zinc dissolution decreases with increasing solution viscosity, but no generally valid threshold value has been found.

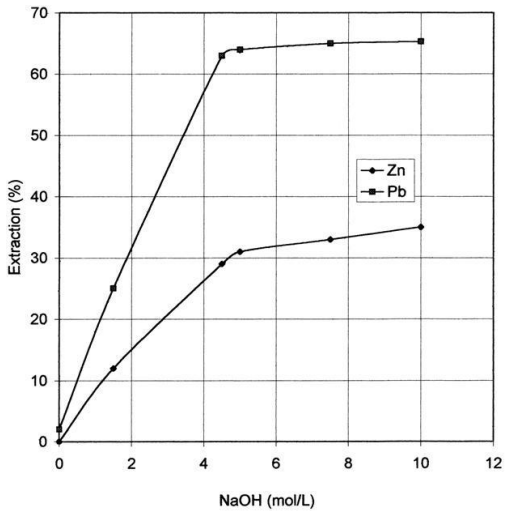
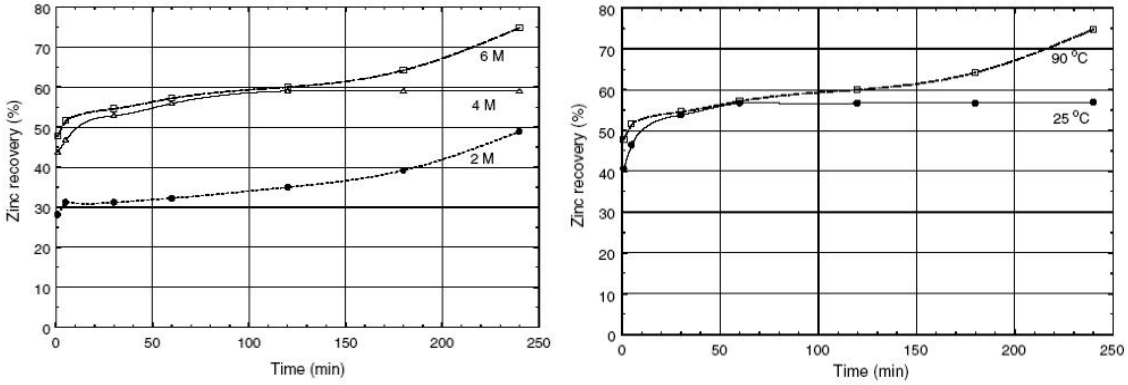


Figure 9. Effect of NaOH concentration on the extraction of Zn and Pb from steelmaking dust (25 °C, L/S 3.6, leaching time 42 h) [11].



a) b)

Figure 10. a) Influence of NaOH concentration on zinc recovery at long leaching times (90 °C). b) Influence of temperature on recovery of zinc at long leaching times (6 M NaOH). [19]

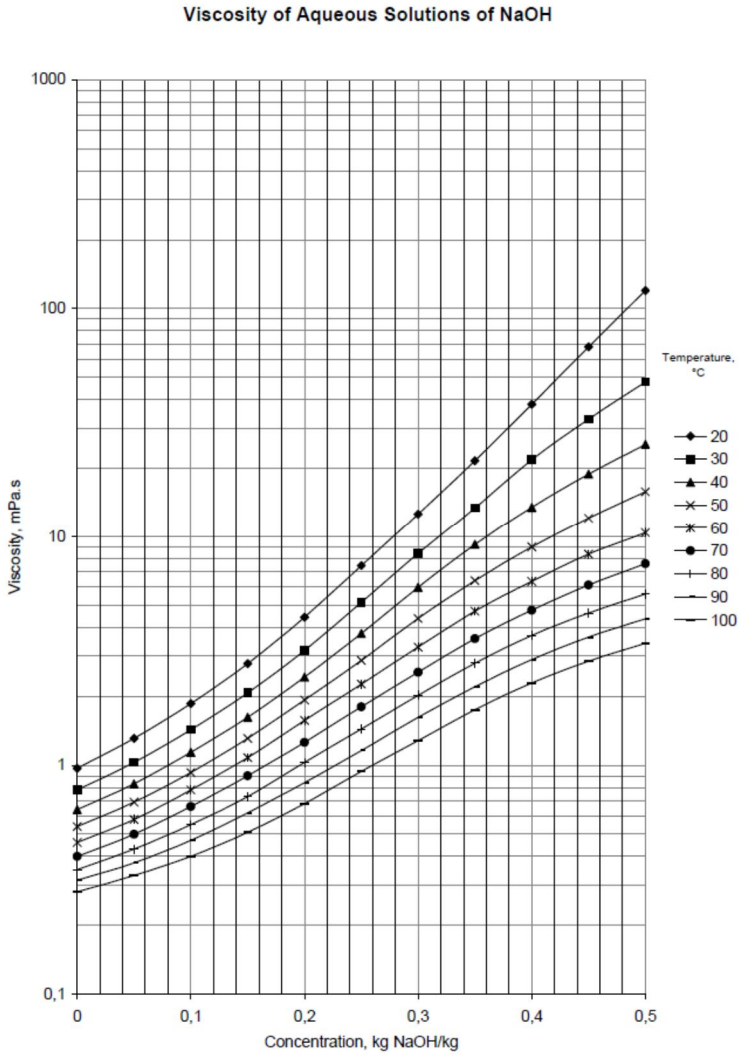


Figure 11. Viscosity of aqueous solutions of NaOH, mPa.s [41].

2.2.2 Particle size, pulp density and agitation

Small particle size and low pulp density (small weight of solids) will favor faster leaching kinetics. The individual particles in the stainless steel production dusts are mostly less than 10 µm so the reaction kinetics involving this kind of material should be fast. The dissolution of soluble forms of zinc is reported to be very fast in caustic soda leaching of steelmaking dusts and leaching times even 30 minutes could be sufficient. [18, 27]

Commonly, the lower is the solid to liquid ration the higher is the recovery percentage. However, it has been reported that no remarkable increase of zinc dissolution have been observed for the S/L ratios above 1/7, when leaching in 10 M NaOH solution for 2 h [28]. Mordogan et al. [1] got the best zinc yield with solid content of 10 %, when using 6.5 M NaOH solution (20 °C, 600 rpm). The solid contents above 20 % have been reported to decrease the recovery of zinc probably due the flocculation of fine dust particles [1, 40]. On the other hand, the solid content have seen to have more effect on leaching time than on the maximum possible zinc extraction that can be obtained if sufficiently strong NaOH solutions is used (Figure 12) [40].

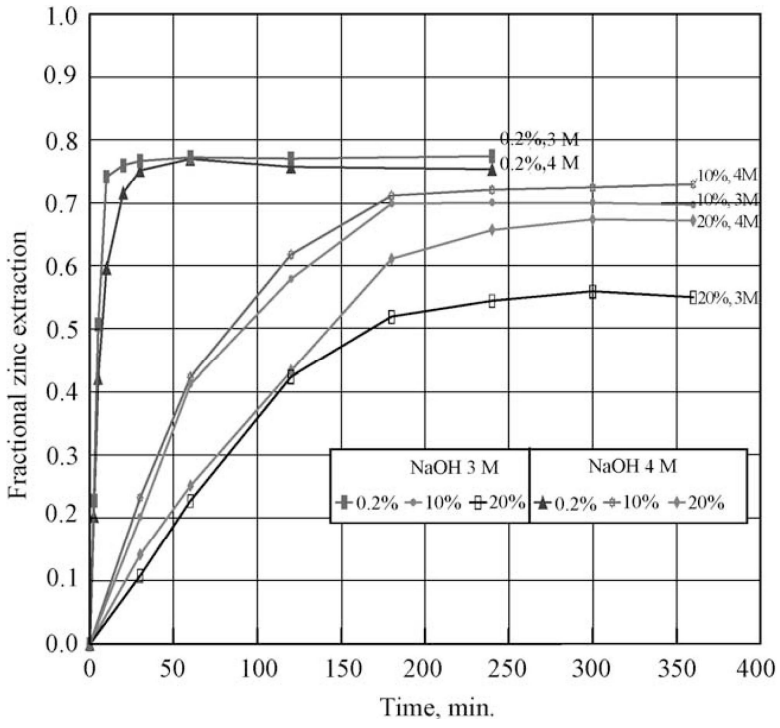


Figure 12. Effect of solid content on leaching rate (850 rpm, 95 °C) [40].

Increasing agitation has seen to increase solubility of zinc from steelmaking dusts as it prevents flocculation. This indicates a relation between solid content and stirring rate. Also when using more viscous solutions (6.5 M NaOH, 40 °C, 10 wt-% solid) the increased stirring rate (from 400 to 900 rpm) increased the solubility of zinc [1]. With more dilute NaOH solutions (1.5 M NaOH, 60 °C, 0.2 wt-% solid) it was found that changing stirring rate between 500 – 850 rpm did not have effect on reaction rate [40].

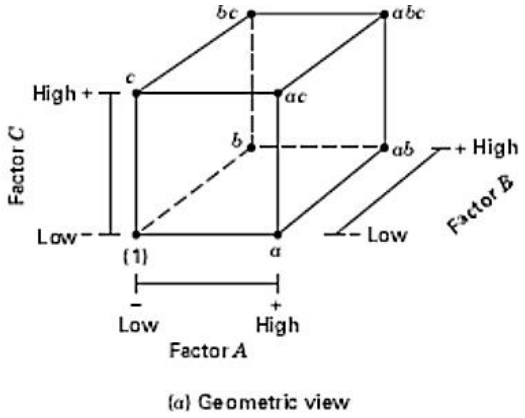
3 DESIGN OF EXPERIMENTS

Commonly the experimental work involves the study of the effects of two or more factors. Factorial design is an important method to determine the effects of multiple factors on a response and, in general, is the most efficient method for this type of experiments. Traditionally, experiments are designed to determine the effect of one variable upon one response. In factorial design the number of experiments to perform can be reduced as the multiple factors are studied simultaneously. [42]

Several special cases of the general factorial design are widely used in research work and form the basis of the designs with considerable practical value. The most important of these special cases is a 2^k factorial design that is particularly useful in the early stages of experimental work when many factors are likely to be investigated. There are k factors, each at only two levels in 2^k designs. These levels may be quantitative (such as two values of temperature, pressure or time) or they may be qualitative (such as two machines, two materials, or the presence and absence of a factor). Because there are only two levels for each factor, it is assumed that the response is approximately linear over the range of the factor levels chosen. This is often a reasonable assumption when just starting to study the process or the system. [42]

The principle of the 2^k designs is illustrated via a 2^3 factorial design in Figure 13. There are three factors, A, B, and C, of interest in the 2^3 factorial design, and the eight treatment combinations can be displayed geometrically as a cube, as shown in Figure 13a. These eight runs are listed in the design matrix (Figure 13b.) by using the "+ and –" notation to represent the low and high levels of the factors. This forms the basic matrix for different variation of 2^k designs. [42]

Factorial design can be used to find main effects of each independent factor and interactions between the factors. The main effect is the average impact or change on the response or output when a factor changes from its low level to its high level. It is calculated as the average output of factors high level minus the average output of its low level.



(a) Geometric view

Run	Factor A	B	C
1	−	−	−
2	+	−	−
3	−	+	−
4	+	+	−
5	−	−	+
6	+	−	+
7	−	+	+
8	+	+	+

(b) Design matrix

Figure 13. a) The geometric view and b) the design matrix of the factorial 2^3 design [42].

Sometimes the effect that one factor has on the output is dependent on the level of another factor and the response is different at the low level of the second factor than at its high level. When this occurs, there is an interaction between the (two) factors. In Figure 14 is demonstrated a) a case when there is no interaction between A and B factors and b) a case when interaction occurs between the factors A and B. [42]

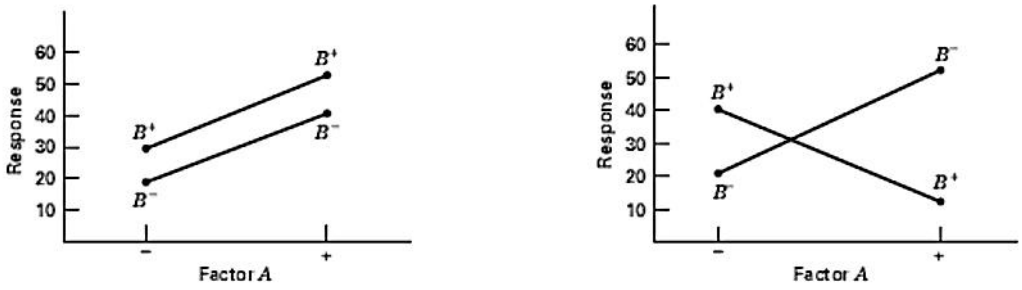


Figure 14. a) A factorial experiment without interaction. b) A factorial experiment with interaction [42].

As the number of factors in a 2^k factorial design increases, the number on runs required for a complete replicate expands very quickly out of the resources of most experimenters. When assuming that some high order interactions are negligible only a fraction of the complete factorial design is needed to run to obtain the information for the main effects and low-order interactions. These fractional factorial designs are mostly used in screening experiments in the early stages of a project when many factors are considered and the objective is to identify those factors that have large effects. The fractional

factorial designs can be projected into stronger (larger) designs to investigate more thoroughly the factors identified as important. [42]

Usually it is reasonable to use fractional designs that have the highest possible resolution consistent with the degree of fractional required. The definitions of the important resolution III, IV and V designs are as follows:

1. *Resolution III designs.* These are designs, in which no main effects are aliased with any other main effect, but main effects are aliased with two-factor interactions and some two-factor interactions may be aliased with each other.
2. *Resolution IV designs.* These are designs in which no main effect is aliased with any other main effect or with any two-factor interaction, but two-factor interactions are aliased with each other.
3. *Resolution V designs.* These are designs in which no main effect or two-factor interaction is aliased with any other main effect or two-factor interaction, but two-factor interactions are aliased with three-factor interactions.

The higher the resolution, the less restrictive are the assumptions regarding which interactions are negligible to obtain a unique interpretation of results. [42]

A one-quarter fraction of the 2^k design is called a 2^{k-2} fractional factorial design. The 2^{k-2} designs may be constructed by first writing down a full factorial design using k – 2 factors and then adding two columns with appropriately chosen interaction involving the first k – 2 factors. This is illustrated in upper part of Table 1 as the resolution III design of 2^{5-2} fractional design. [42]

By combining fractional factorial designs in which certain signs are switched, it is possible to systematically isolate effects of potential interest. This type of sequential experiment is called fold over of the original design. For example resolution III designs can be elevated to resolution IV by adding a second fraction in which the signs for all the factors are reversed (Table 1). This type of fold over is sometimes called a full fold over or a reflection. It breaks the alias links between all the main effects and their two-factor interactions and all the main effects can be estimated clear of any two-factor interactions. [42]

Table 1. A 2^{5-1}(IV) design obtained by fold over the original 2^{5-2}(III) design [42].

Original 2^{5-2}(III) design				
Basic design				
A	B	C	D = AB	E = AC
-	-	-	+	+
+	-	-	-	-
-	+	-	-	+
+	+	-	+	-
-	-	+	+	-
+	-	+	-	+
-	+	+	-	-
+	+	+	+	+
Second 2^{5-2}(III) design with signs switched				
A	B	C	D = -AB	E = -AC
+	+	+	-	-
-	+	+	+	+
+	-	+	+	-
-	-	+	-	+
+	+	-	-	+
-	+	-	+	-
+	-	-	+	+
-	-	-	-	-

The sequential use of fractional factorial designs is very useful, often leading to great economy and efficiency in experimentation. It is almost always preferable to run a fractional design, analyze the results, and then decide on the best set of runs to perform next. If it is necessary to resolve ambiguities, the alternate fraction can be run and complete the design. The fractional factorial designs are among the most widely used types of designs for product and process design and for process improvement. For a moderately large number of factors, smaller fractions of the 2^k design are frequently useful. Resolution III designs can be very reasonable in these situations when there are relatively many factors but only a few of them are expected to be important. [42]

4 MATERIALS AND METHODS

Dust samples for the leaching experiments were received from stainless steel production at Outokumpu Tornio Works. The studied dust samples in this thesis included argon-oxygen decarburization (AOD) converter dusts and electric arc furnace (EAF) dusts from two production lines. AOD1 and EAF1 dusts are generated from production line 1 that uses molten ferrochrome whereas AOD2 and EAF2 are from line 2 in which solid ferrochrome is melted along with the charge. Line 1 is used for production of nickel-free ferritic grades and demanding austenitic grades. In line 2 are produced standard austenitic grades using alloyed recycled steel.

4.1 Composition of dusts

The studied dust samples were collected from baghouse filter containers and they are mixtures of different production batches representing an average dust composition. 200 kg batches were collected in a sample campaign during fall 2009. The batches were homogenized and divided to 1 kg samples. The characterization of the dusts was carried out by University of Oulu, Technical University of Kosice and Labtium Oy.

The particle size analysis of dust samples was performed with Scanning-Foto-Sedimentograf (Fritsch GmbH). The size distributions from the analysis are presented in Table 2 and in Figure 15 are shown the cumulative and distribution curves of particle sizes. The results showed that the studied dusts have very similar granulometry and the particle sizes of the dusts were from less than 1 µm to around 50 µm. The microstructure of the dusts consists of larger particles and grains surrounded by finer fraction that is also verified in Figure 16. The larger particles were usually in size range of 27 µm to 47 µm. Also agglomeration of finer fraction was noticed. Especially for AOD2 dust, from the distributive curves can be seen that there are two major fractions in particle sizes. [43, 44]

Table 2. Size distribution of dust samples [43].

	AOD1	AOD2	EAF1	EAF2
< 1 µm	1.5	0.9	---	1.4
< 2 µm	12	7	1.6	5.5
< 8 µm	25	16	13	20
< 16 µm	38	36	27	36
< 22 µm	52	46	42	50
< 28 µm	62	56	61	65
< 40 µm	85	83	85	84
< 47 µm	100	100	94	93
< 50 µm	---	---	100	97
< 53 µm	---	---	---	100
Q(10)	27	19	10	23
Q(40)	85	83	85	84
Q(63)	100	100	100	100

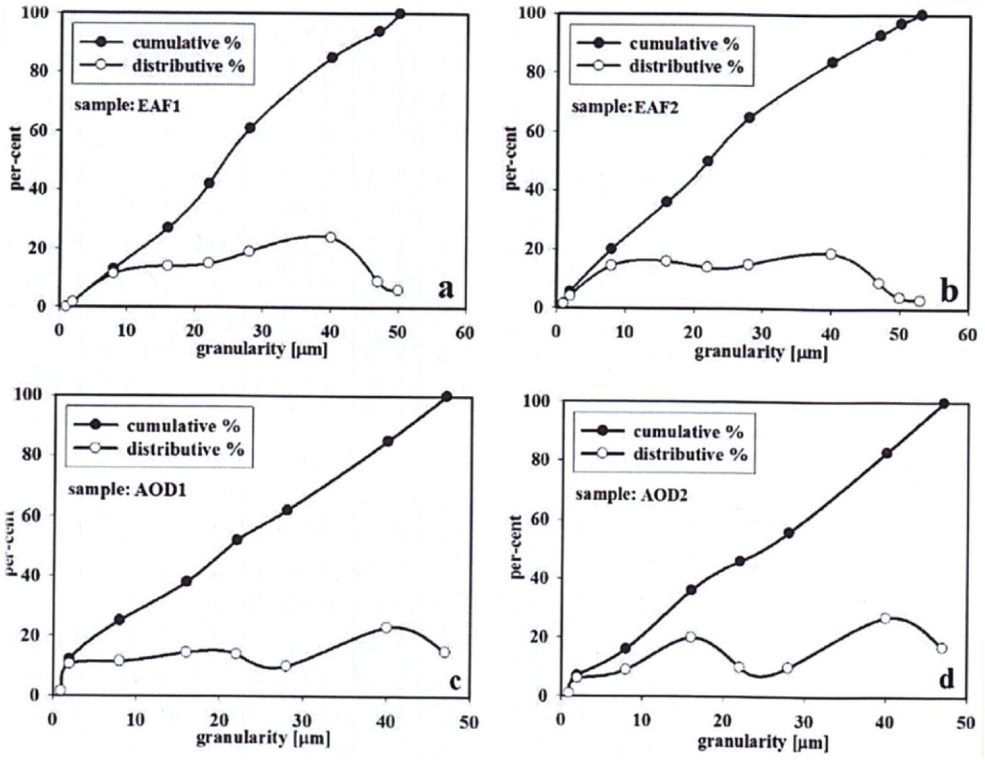


Figure 15. Cumulative and distributive curves of the dust samples [44].

The chemical and mineralogical characterization was performed by optical microscopy, Scanning Electron Microscope (SEM), Electron Probe Micro-Analyzer (EPMA), X-Ray Diffraction (XRD), Atomic Absorption Spectroscopy (AAS), and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) with molten sodium peroxide or nitro-hydrochloric acid leaching pre-treatment. The average compositions of the dusts are

presented in Table 3. The main elements in the dusts are iron, chromium, zinc and calcium. Dusts contained also some Mo, Mn, Mg, Ni and Si, and minor amounts many other elements. The element with highest variation is chromium of which it was found that only a third will dissolve in sample pretreatment with nitric and hydrochloric acid but it was broken down in molten sodium peroxide. Also iron had high variation compared with the other elements.

Table 3. The chemical composition of the dusts samples.

	Fe	Cr	Zn	Ca	Mn	Ni	Mg [a]	Si [b]
AOD1	33.03 ± 2.26	9.18 ± 2.67	9.76 ± 0.31	5.07 ± 0.15	2.41 ± 0.71	0.6 ± 0.06	1.30 ± 0.05	0.89
AOD2	21.51 ± 2.39	7.51 ± 2.25	4.65 ± 0.42	15.18 ± 0.66	2.28 ± 0.49	2.51 ± 0.18	1.49 ± 0.02	2.76
EAF1	19.75 ± 1.64	8.07 ± 3.03	7.27 ± 0.54	10.35 ± 0.46	2.47 ± 0.45	1.28 ± 0.14	2.59 ± 0.15	4.25
EAF2	16.39 ± 1.84	8.10 ± 2.95	5.20 ± 0.58	13.48 ± 0.72	2.14 ± 0.40	2.14 ± 0.23	0.75 ± 0.13	4.11
Minor amounts 0 - < 1 % in all dusts	Al, B, Ba, C, Cd, Co, Cu, F, Mo, Na, P, Pb, S, Sr, V Exceptions: 1.36 ± 0.02 % Mo in AOD2 dust and 1.32 ± 0.04 % K in EAF1 dust							

[a] calculation is based on three separate analyses [b] found only in one analysis

The main compounds identified in the dusts from qualitative phase analysis are presented in Table 4. According to XRD analysis, all dust samples are very similar in mineralogical composition. The main phases present in the dusts are oxides of CaO, ZnO and Fe_2O_3 and spinels of $FeCr_2O_4$, $ZnFe_2O_4$, and $Ni_{0.25}Fe_{0.75}Fe_2O_4$. As can be seen in Table 4, zinc was found to be present as zincite (ZnO) and franklinite ($ZnFe_2O_4$). Nickel is present as a spinel compound $(NiFe)Fe_2O_4$ and chromium is present in all dusts mainly as chromite, $FeCr_2O_4$. Regarding the XRD analysis it should be noted that the XRD spectra of ferrites are very similar what makes difficult to distinguish what kind of ferrite is present in the sample. Especially the spectrum of franklinite is largely overlapping with the spectrum of magnetite. Because of the large number of identified compounds and uneven distribution of the elements to different phases a quantitative mineralogical analysis could not be determined. [44]

Table 4. The main phases identified in each sample from XRD analysis [44].

EAF1	EAF2	AOD1	AOD2
$FeCr_2O_4$	$FeCr_2O_4$	$FeCr_2O_4$	$FeCr_2O_4$
$ZnFe_2O_4$	$ZnFe_2O_4$	$ZnFe_2O_4$	$ZnFe_2O_4$
$Ni_{0.25}Fe_{0.75}Fe_2O_4$	$NiFe_2O_4$	$ZnCr_2O_4$	$Ni_{0.25}Fe_{0.75}Fe_2O_4$
ZnO	CaO	Fe_3O_4	ZnO
CaO	$CaCO_3$	Fe_2O_3	$CaCO_3$
	MnO_2	ZnO	$Ca(OH)_2$

Optical microscope pictures of the dust samples are shown in Figure 16. The pictures and EPMA analysis showed that larger particles often consist of several phases and some phases were encapsulated inside of particles. All dusts contained Cr-Fe-oxide –particles in which the share of FeO and Cr_2O_3 varied. In AOD dusts were also spherical particles with Cr-Fe-oxide cover and chromite interior. It was also found that there are grains consisting of one or several phases, as intrusions in glass in the larger particles. For example chromite and magnesiochromite phases occurred as instructions in glass. Also homogenous grains of one phase were found. The microstructure of the fine particle fraction remained still unknown as they do not stand out even with SEM. However, it can be stated that sometimes zinc was found to be concentrated in finer fraction of the dusts. [45]

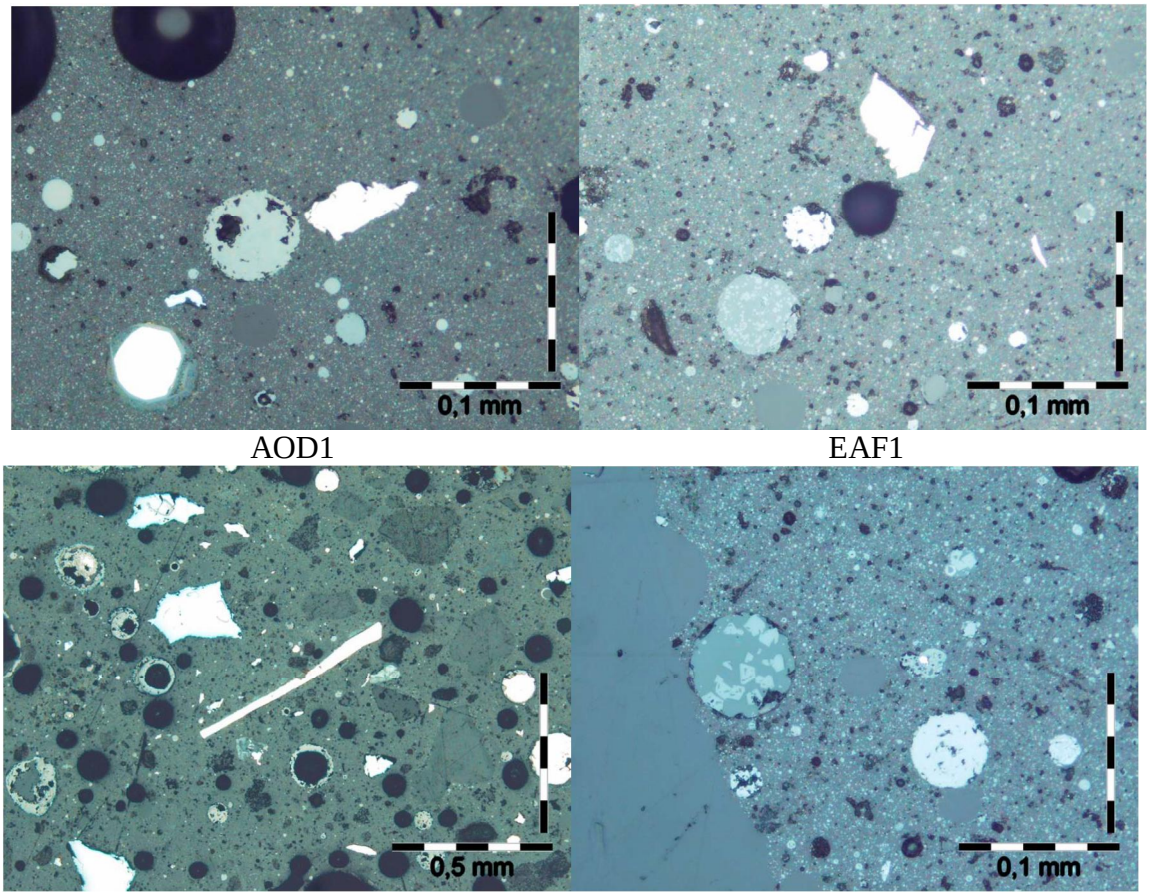


Figure 16. Optical microscopy pictures of received dust samples [45].

4.2 Leaching experiments

The leaching tests were performed using fractional factorial designs. In this method several factors are changed simultaneously in order to find out the most important factors and the possible interactions of the factors. Interactions are not found if only one factor would be changed at a time. A base design for all dusts was a 2^{5-2} fractional factorial design described in the publications [I-IV] and for AOD1 and EAF1 dusts also a fold-over of the original design was run (Table 5). The Minitab software was used for planning the experimental layout and for the interpretation of the results.

The studied factors were temperature, NaOH concentration, liquid-solid ratio (ml/g), stirring rate and oxygen/nitrogen gas bubbling. The extreme values of factors range were chosen to be certain that the factors will have clear effect. The used temperatures were 25 °C and 95 °C, and concentrations of NaOH solutions were 2 M and 8 M. The chosen liquid/solid (ml/g) ratios were 5 and 30, and stirring rate was adjusted to 100 or 400 rpm. In the choice of higher value of temperature and stirring rate were considered the physical limits of the reactor system.

Table 5. Test series used in the leaching experiments.

2^{5-2} factorial test series						Fold-over series					
Std Order	NaOH (M)	L/S Ratio	Temp. ºC	Bubbling with	Agitation Rpm	Std Order	NaOH (M)	L/S Ratio	Temp. ºC	Bubbling with	Agitation Rpm
1	2	5	25	O_2	400	8	2	5	25	N_2	100
2	8	5	25	N_2	100	7	8	5	25	O_2	400
3	2	30	25	N_2	400	6	2	30	25	O_2	100
4	8	30	25	O_2	100	5	8	30	25	N_2	400
5	2	5	95	O_2	100	4	2	5	95	N_2	400
6	8	5	95	N_2	400	3	8	5	95	O_2	100
7	2	30	95	N_2	100	2	2	30	95	O_2	400
8	8	30	95	O_2	400	1	8	30	95	N_2	100

The experimental setup (Figure 17) for the leaching tests consisted of a termobath (Lauda AquaLine AL25), glass reactor and motor driver stirrer (VWR VOS16). The lid of glass reactor provided through holes for mercury thermometer, gas bubbling, stirrer and sampling/feeding. A water-cooled condenser was used at higher temperatures. NaOH

solutions were prepared from technical grade grains and distilled water, and a volume of 800 ml was set into reactor. Temperature of the reactor was controlled with a water bath. For adjusting the oxidative or reductive conditions, oxygen or nitrogen gas was fed into the reactor for 1 hour and after that 26.67 or 160 g of dust (liquid/solid ratios of 30 and 5) was charged and stirring rate was adjusted.

A liquid sample was taken off and filtered in the chosen time intervals of 5, 10, 15, 20, 25, 30, 60 and 120 minutes for AOD1 and EAF1 dusts and 5, 15, 30, 60 and 120 minutes for AOD2 and EAF2 dusts. The stirring was stopped 30 seconds before each sampling.

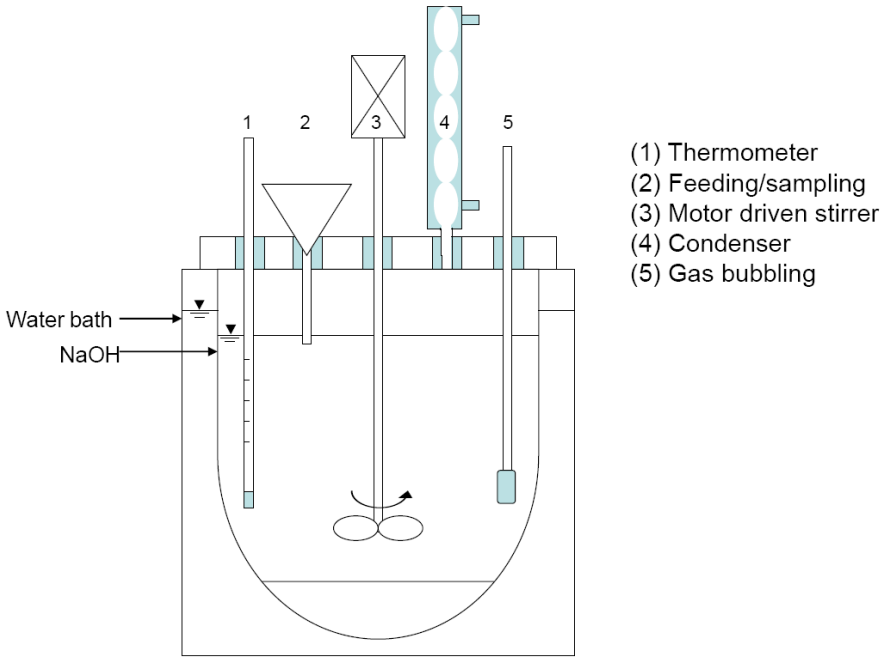


Figure 17. A schematic presentation of the leaching reactor in water bath [I,III].

After filtering the leach samples were analyzed for amount of leached Zn with Perkin Elmer 372 AAS device. The standard solutions were prepared by using Atomic Absorption Standard zinc 1000 µg/ml Baker 6827 solution. As the most stable area for the measurements is around 0.4 – 1.6 ppm [46], the leaching experiment samples were diluted to reach this area with two-phase dilution to ratio of 1:100 – 1:15000 depending on the zinc content in the leach samples. When diluting the leach samples nitric acid

addition was used in order to keep pH low enough and thereby to ensure that zinc will not precipitate.

Part of the samples after 120 min of leaching was analyzed more precisely with multi-element ICP-AES analysis in order to investigate what other elements were leached with zinc and to confirm that the unwanted iron were not leached. The analyzed leach samples of AOD1 dust were from the experiments (std orders) 1, 2, 3, 7, 8, 11 and 12 from 2^{5-2} series and 1, 6, 11, 12, 15 and 16 from the fold-over series. The analyzed samples of EAF1 dust were from the experiments 6, 11, 12 and 14 from 2^{5-2} series and 6, 11, 12 and 16 from the fold-over series. In case of AOD2 and EAF2 dusts all the samples after 120 min leaching were analyzed with ICP-EAS.

5 RESULTS

In this chapter the results from the experimental work is presented. The main response under investigation was the percentage of zinc extraction from stainless steel AOD and EAF dusts in the leach liquor. The factorial design and analysis of the experiments were used in order to determine the main effects and interactions of the leaching factors. Also the solubility of certain elements was investigated from the leach samples to confirm the selectiveness of alkaline leaching in dissolving zinc. The results presented in this chapter rest upon the publications [I-IV] but also contain the supplement information that the fold-over series has brought out.

5.1 Dissolution of zinc

Figure 18 shows the leaching curves of AOD1 dust from 2^{5-2} fractional factorial experiments from which can be seen the general leaching behavior of zinc in NaOH solution. The shapes of leaching curves were similar for all studied dusts. It was observed that dissolution of zinc was fast occurring in few minutes, and then increased only slightly in most cases [I-IV]. In few experiments the maximum yield of zinc was achieved earlier and then was decreased slightly. Usually, the maximum yield was achieved at the end of test, which was after 120 min of leaching. The leaching conditions affected the amount of extracted zinc but the shape of curves were pretty similar, zinc was dissolved fast in leaching conditions that resulted high or low zinc dissolution.

Table 6 shows the results for zinc extraction after 120 min leaching from both test series. Under the present experimental conditions, zinc extraction varied from 6 % to around 80 % for AOD1 dust, from 13 % to 51 % for AOD2 dust, from 8 % to 60 % for EAF1 dust and from 8 % to 34 % for EAF2 dust. The extractions were on the average lower for dusts from line two (AOD2 and EAF2) and from both lines the extractions were greater from AOD dust. The general trends that can be observed from the Table 6 are that the dissolution of zinc is increased with higher NaOH concentration and temperature. Also strong agitation is favorable.

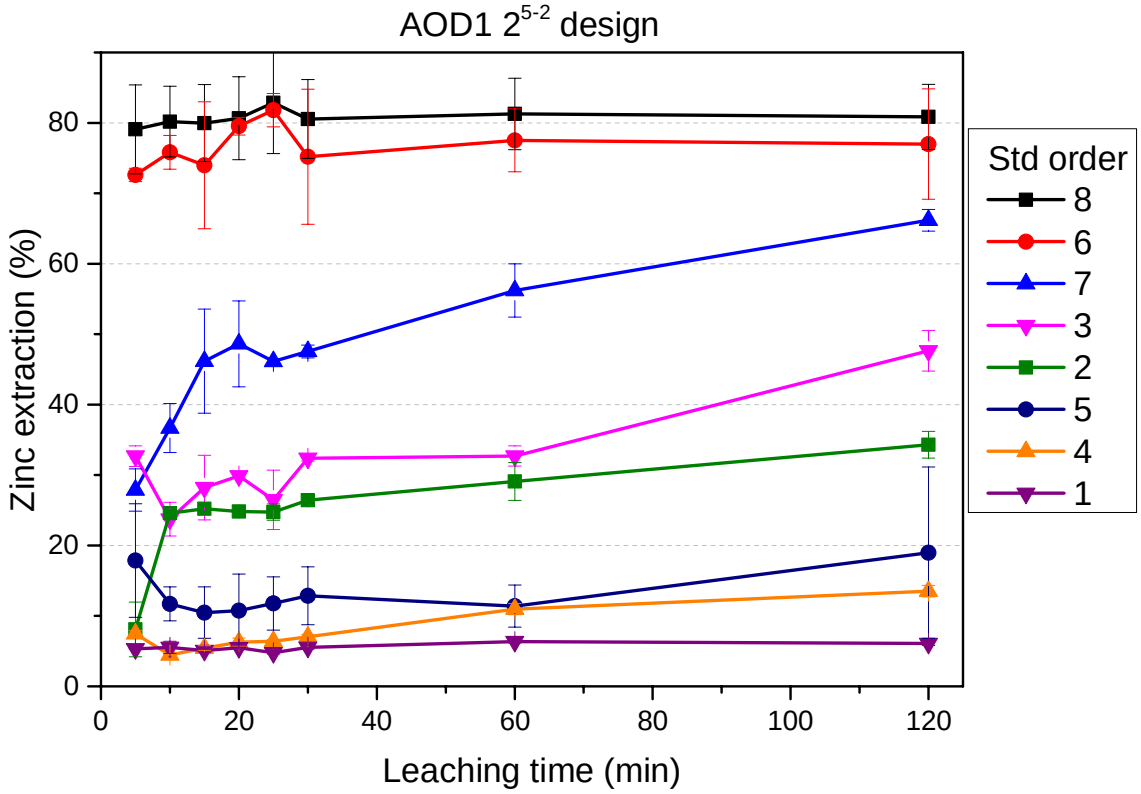


Figure 18. The leaching curves of zinc dissolution from AOD1 dust according to results from 2^{5-2} design.

As shown in Table 6 there were two leaching conditions in the test series in which zinc extraction was greatest for all four dusts [I-IV]. In both tests strong 8 M NaOH solution with high temperature and stirring rate was used, but the bubbling gas and liquid to solid ratio changed. Almost equivalent zinc extraction was achieved with these two leaching conditions. The fold-over test series were not done for AOD2 and EAF2 dusts but the two best leaching conditions are both in the original 2^{5-2} factorial test series.

Table 6. Results for zinc dissolution after 120 min leaching from AOD1, AOD2, EAF1 and EAF2 dusts.

NaOH, M	L/S Ratio	Temp., Deg C	Bubbling with	Agitation Rpm	Recovery (%) after 120 min leaching			
					AOD1	AOD2	EAF1	EAF2
8	*30*	*95*	*O_2*	*400*	*80,85*	*51,45*	*60,75*	*31,70*
8	30	95	N2	100	77,12	-	37,87	-
8	*5*	*95*	*N_2*	*400*	*76,99*	*49,30*	*58,04*	*33,62*
2	30	95	O2	400	72,50	-	41,17	-
2	30	95	N_2	100	66,17	40,34	21,32	16,07
8	5	95	O2	100	61,97	-	15,31	-
8	30	25	N2	400	60,54	-	32,91	-
8	5	25	O2	400	*50,13*	-	27,27	-
2	30	25	N_2	400	47,65	34,76	23,51	14,90
8	5	25	N_2	100	34,30	27,01	19,39	11,51
2	5	95	N2	400	20,93	-	21,81	-
2	5	95	O_2	100	18,98	24,58	20,55	12,10
8	30	25	O_2	100	13,53	12,70	18,40	8,17
2	5	25	N2	100	11,42	-	7,89	-
2	30	25	O2	100	7,88	-	7,68	-
2	5	25	O_2	400	6,10	23,98	13,71	10,65

The leaching curves of zinc in the two leaching conditions with highest recoveries are shown in Figure 19 showing that for all studied dusts the dissolution of zinc is fast and the most of the leachable zinc is dissolved in few minutes. The maximum amount of extracted zinc was greater with the dust from line 1 and zinc was dissolved better from AOD dust than from the EAF dust when comparing the dusts from the same line. In case of AOD1 dust there was also a third leaching condition that gave around same zinc extraction after 120 min of leaching. In this temperature and NaOH concentration were also at high level but the low level of agitation was used and the amount of dissolved zinc increased slower with time.

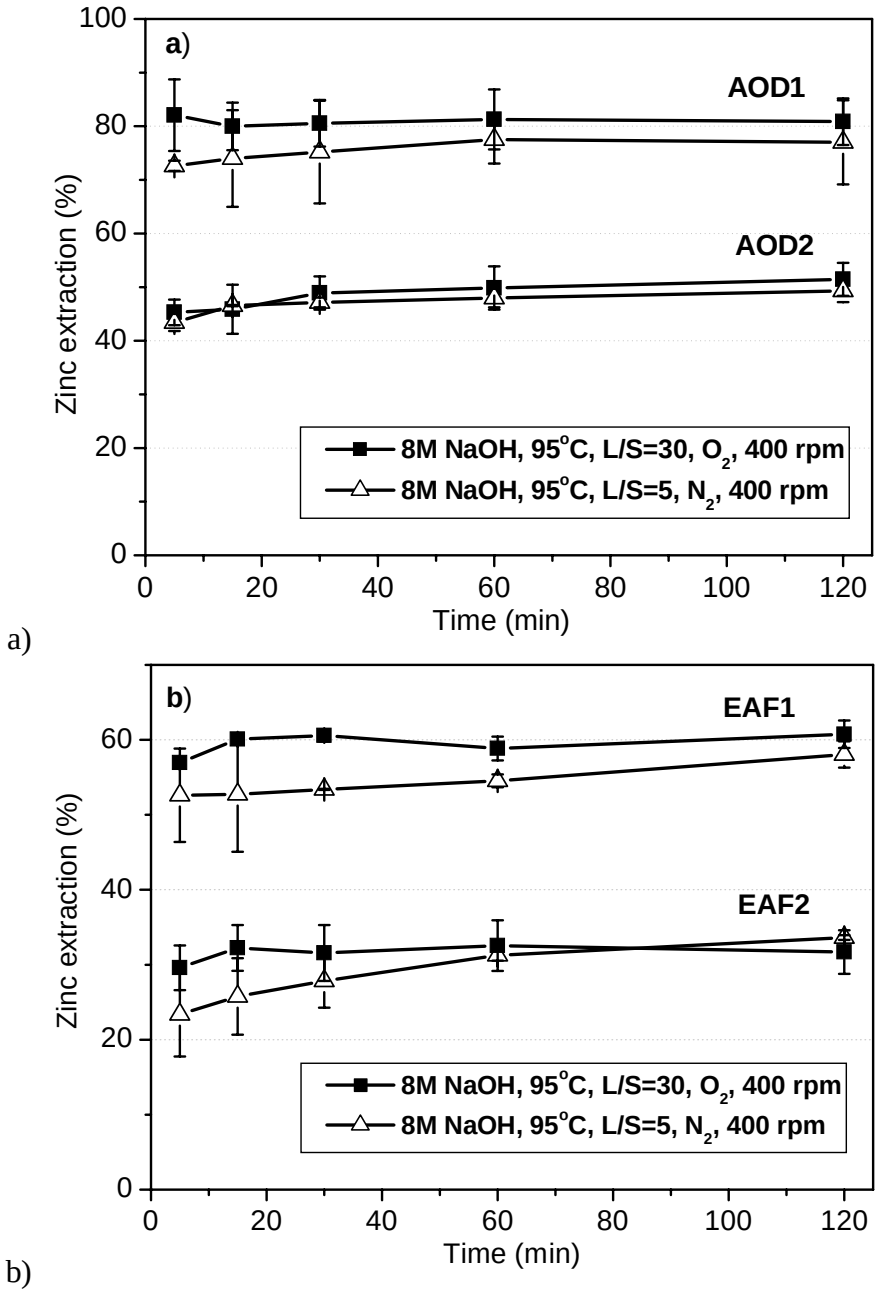
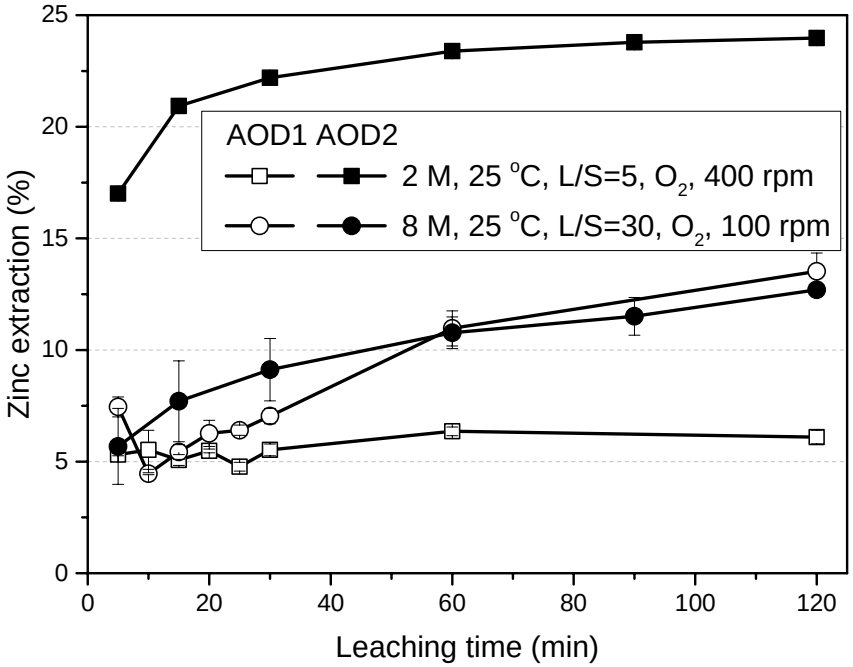


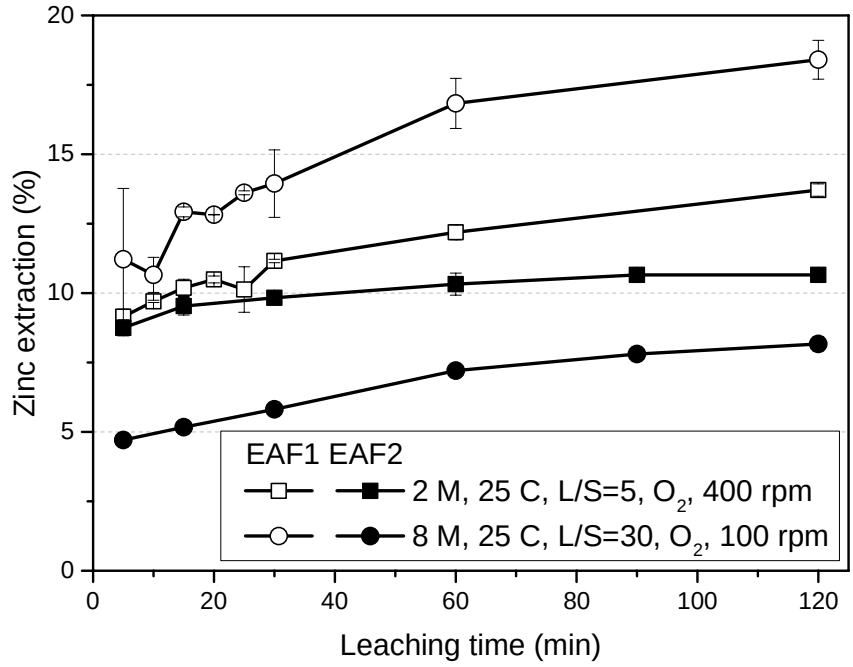
Figure 19. The leaching curves of zinc from the experimental conditions in which zinc extraction was greatest. a) AOD dusts b) EAF dusts. [II]

Figure 20 shows examples of leaching curves of zinc dissolution from two different leaching conditions in which poor extractions were obtained. In these conditions leaching was also quite fast for all dusts and increased only slightly with time. There was more variation with the least effective leaching conditions than with those that gave highest

zinc extractions between the dusts. One common factor with the least effective ones was low temperature but the other factors fluctuated.



a)



b)

Figure 20. Example of the leaching curves when low zinc extractions were obtained. a) AOD dusts b) EAF dusts.

5.2 The effect of leaching factors

In order to investigate the main effects of the studied leaching factors, the zinc extraction results after 120 min leaching were analyzed using the Minitab software. The Minitab software was also used to find the possible interactions of studied factors.

5.2.1 Main effects

The main effects of EAF dust leaching are reported in publication IV and those of AOD dusts in publication III. Figure 21 and Figure 22 show additional information in the form of main effect and Pareto charts for AOD1 and EAF1 dust from 2^{5-2} fractional factorial and fold-over test series. High or deep slope in the main effect chart describes stronger effect of the factor and also tells the response direction. In Pareto charts the vertical red line is founded on the current error estimate and the factors above are seen as statistically significant.

From the charts in Figures 21 and 22 can be observed that temperature and NaOH concentration were statistically strongly significant factors on zinc dissolution for AOD1 and EAF1 dusts. Agitation speed and L/S ratio were also statistically significant factors and for EAF1 dust, the agitation speed had even the strongest effect. The response was positive for all the studied quantitative factors and the dissolution of zinc was enhanced with increasing level of those. Gas bubbling was a qualitative factor and oxygen gas bubbling had a negative response and the dissolution of zinc was enhanced with nitrogen gas bubbling. Despite that, the highest zinc extraction was achieved at conditions in which oxygen bubbling was used, as the significance of the other factors was stronger. In case of EAF1 dust the effect of bubbling gas was not statistically even significant. The gas bubbling was expected to change the redox-potential of the solution. The results indicate that the dissolution mechanism is not electrochemical and this not affected by oxidizing (O_2 bubbling) or reducing (N_2 bubbling) conditions.

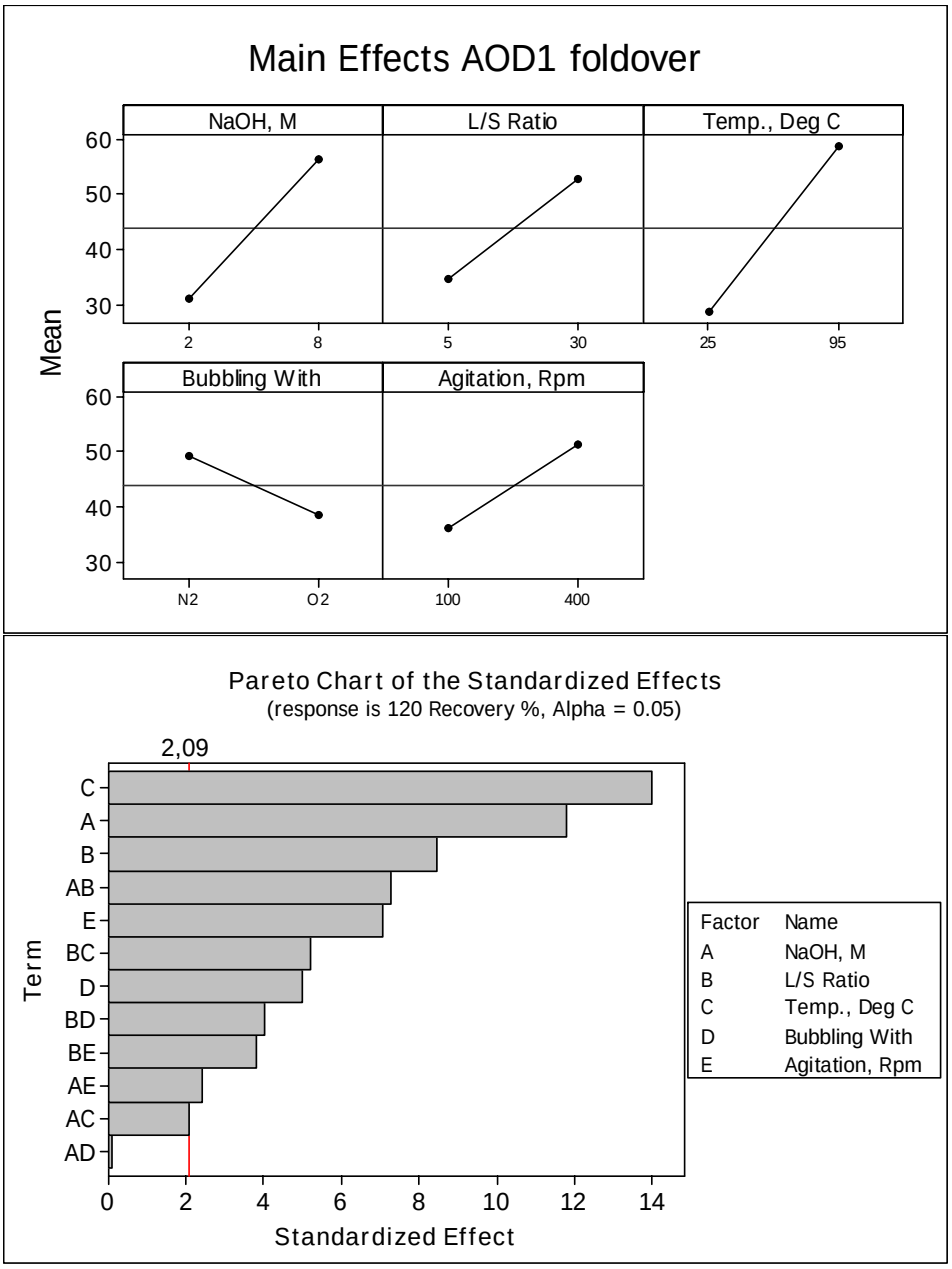


Figure 21. The main effect and the pareto charts of the studied factors for AOD1 dust.

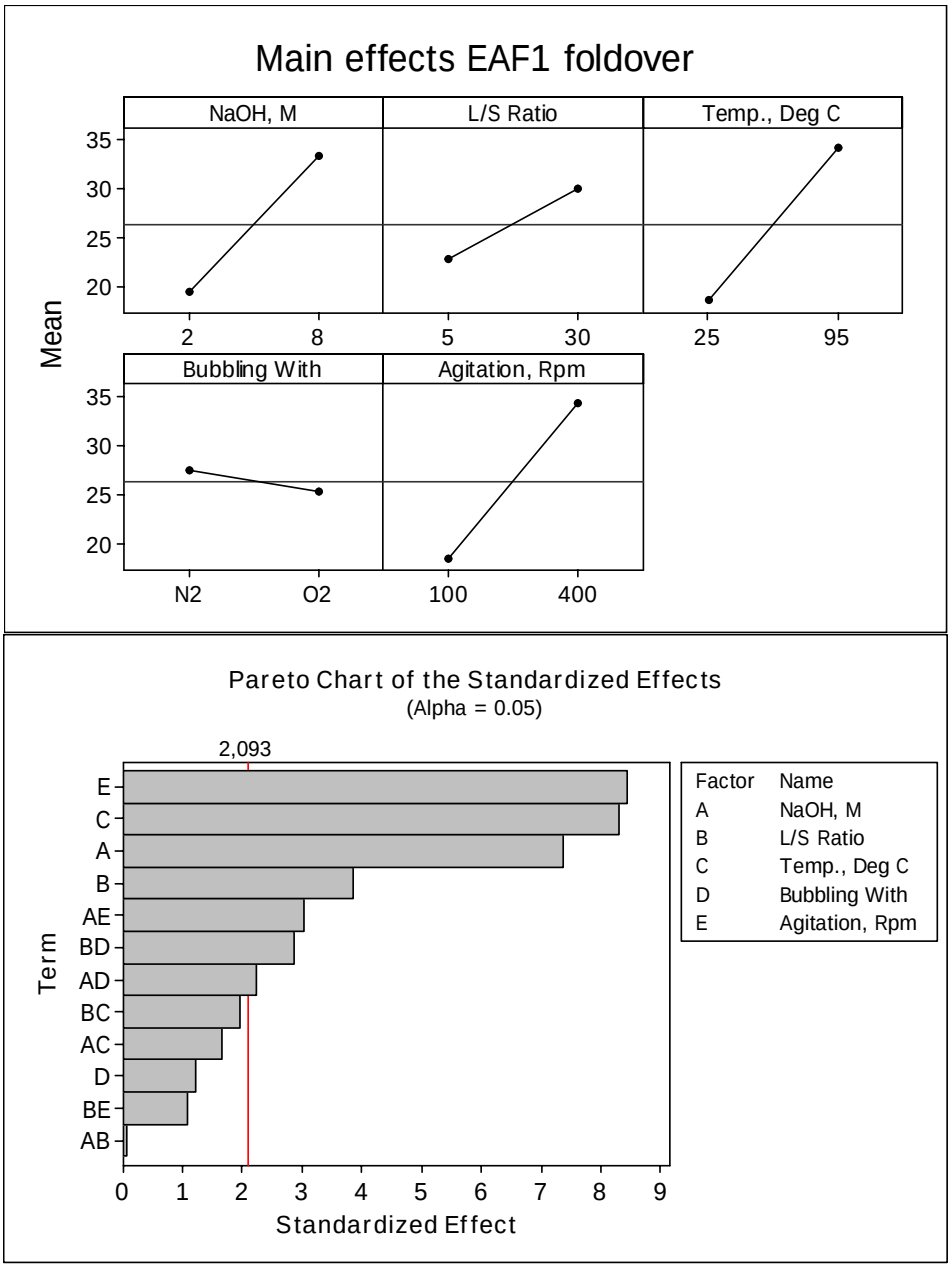


Figure 22. The main effect and the pareto charts of the studied factors for EAF1 dust.

The main effect and Pareto charts from the 2^{5-2} fractional factorial test series for AOD1 and EAF1 dusts are shown in Figure 23 and Figure 24, and similarly for AOD2 and EAF2 dusts in Figure 25 and Figure 26. The results were pretty similar for the dusts from line 2 as the ones from line 1. The increasing level of the quantitative factors and nitrogen gas bubbling enhanced the zinc dissolution [III,IV]. The same three factors (temperatute, agitation speed and NaOH concentration) were distinctly significant factors for the EAF dusts. The L/S ratio was insignificant factor for EAF2 [IV], but after the fold-over series its effect in case of EAF1 dust was slightly increased. In case of AOD2 the all studied leaching parameters were statistically significant [III] likewise for AOD1. Some differences occurred in significance order; the effect of agitation speed was more emphasized for AOD2 dust whereas the impact of NaOH concentration was lower. For AOD1 dust L/S ratio and NaOH concentration were more significant factors.

When contemplating these results from analysis with Minitab software, it should be noted that the effect of factors are confounded with interactions and thus the calculated effect is actually the combination of one factor plus the effects of confounded two-factor interactions. For example, NaOH concentration is confounded with interactions L/S ratio*bubbling gas + temperature*agitation speed in 2^{5-2} series (the effect of NaOH = A + BD + CE) and after the fold-over experiments this confounding is eliminated.

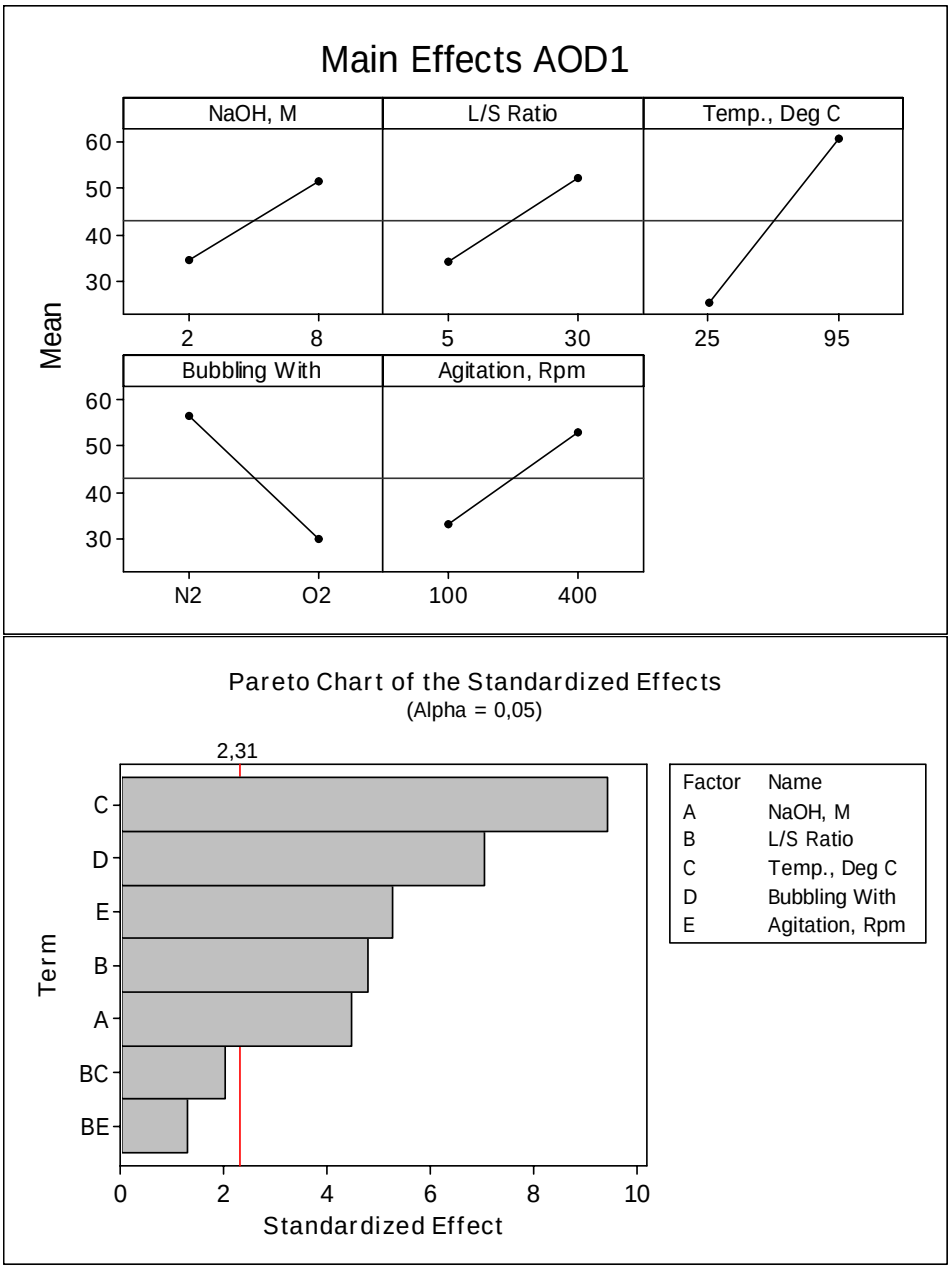


Figure 23. The main effects and the standardized effects of the studied factors for AOD1 dust when only 2^{5-2} factorial test series was performed.

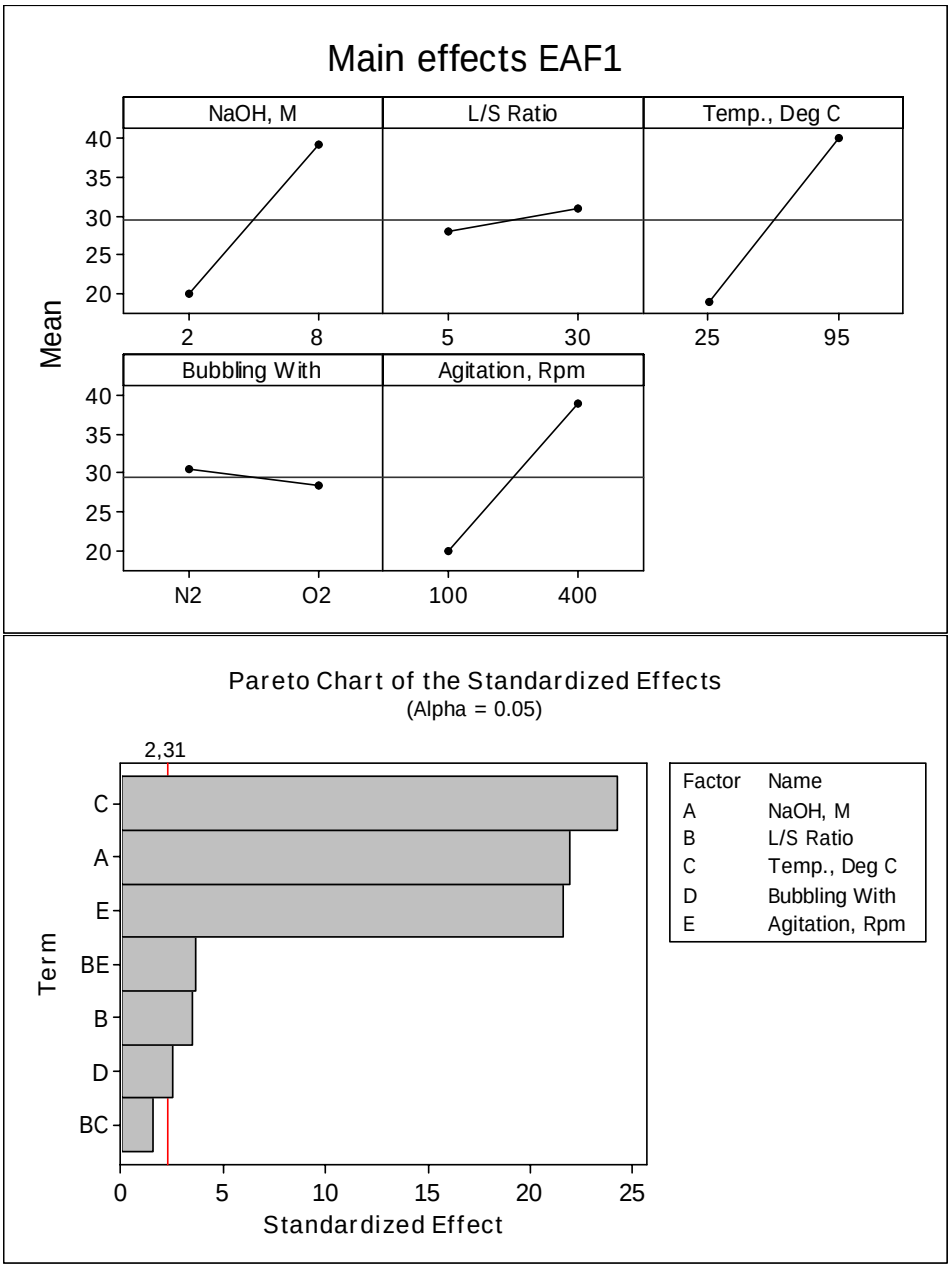


Figure 24. The main effects and the standardized effects of the studied factors for EAF1 dust when only 2^{5-2} factorial test series was performed.

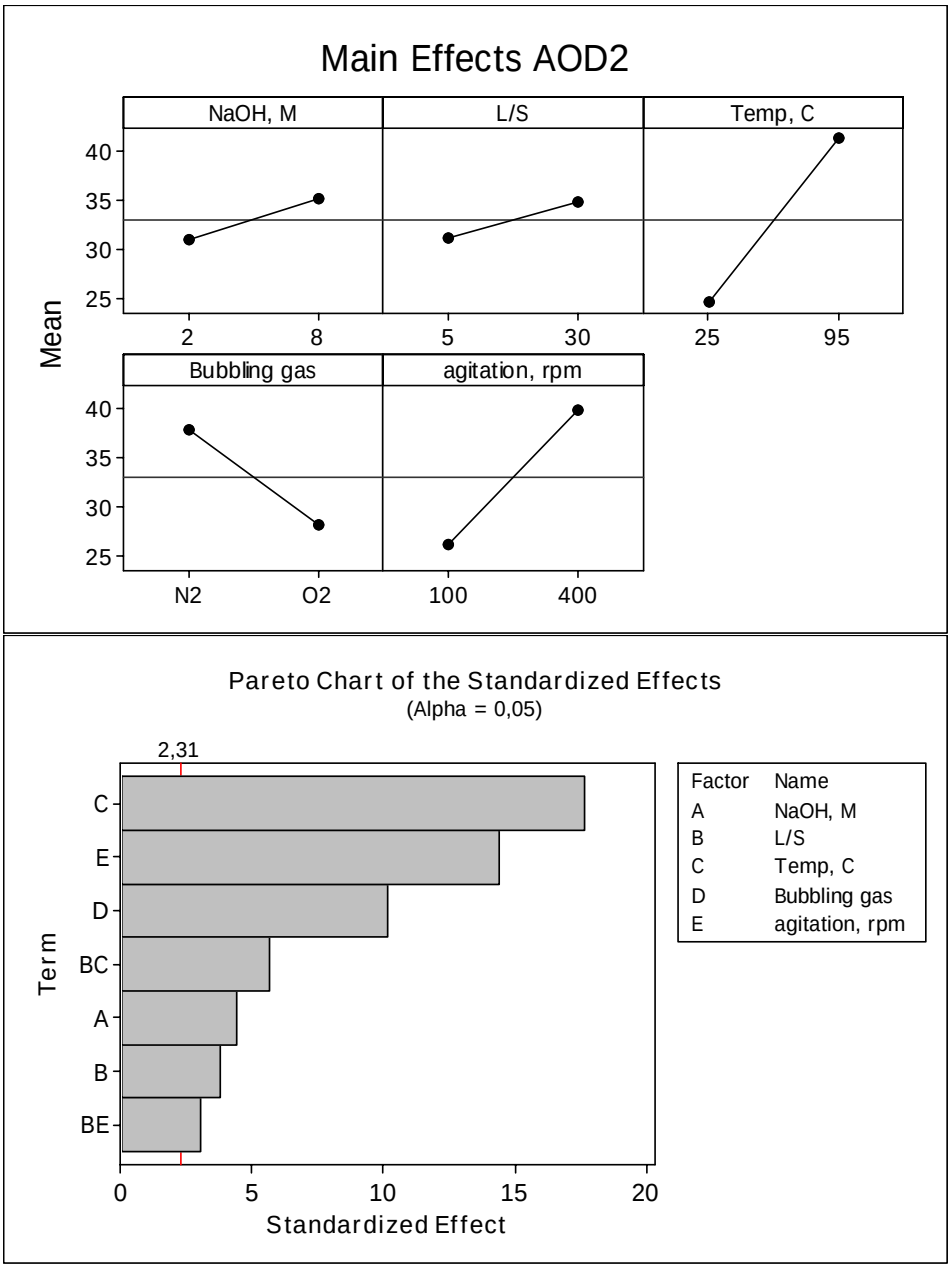


Figure 25. The main effects and the standardized effects of the studied factors for AOD2 dust.

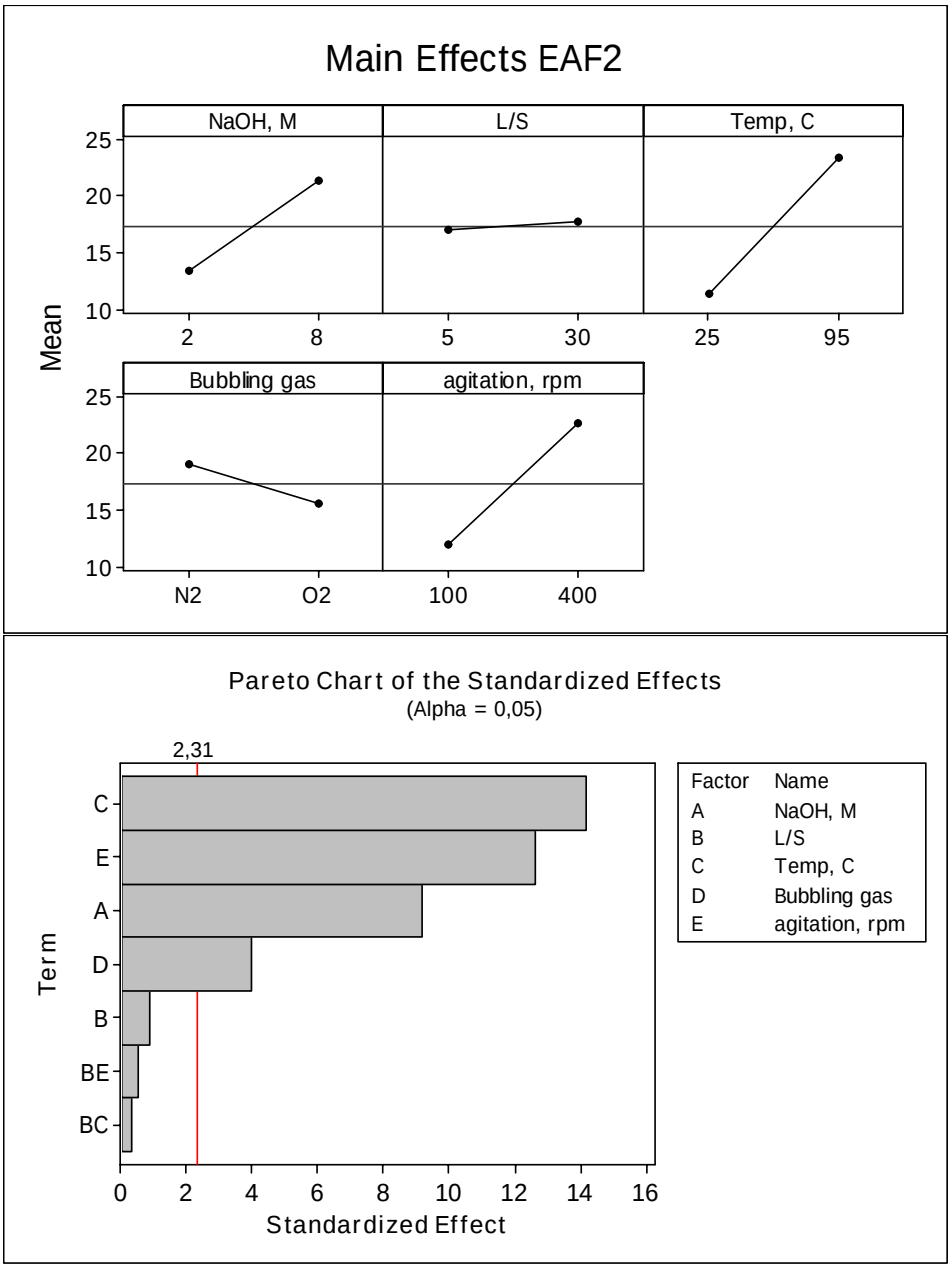


Figure 26. Main effects and standardized effects [IV] of the studied dusts for EAF2 dust.

5.2.2 Interactions

Figure 27 and Figure 28 show the interaction charts for AOD1 and EAF1 dusts after both test series whereas the interaction charts in Figures 29 – 32 are from the 2^{5-2} design experiments. In determination the extractions after 120 min leaching were used. Interaction between the factors occurs when the effect that one factor has on the output is dependent on the level of another factor and the response is different at the low level of the second factor than at the high level of the second factor. Interactions between the factors can be seen when the slopes are non-parallel.

When comparing the results after fold-over series with results when only 2^{5-2} design was performed, there seems to be more interactions between the factors in the interaction charts when only 2^{5-2} design is performed. In other words, more lines that are non-parallel or crossed can be seen. When the fold-over series were also performed and combined, the lines in the interaction charts are more parallel. Because the results after the 2^{5-2} design were very similar for dust from the same type of furnace, it can be assumed that if a fold-over leaching test is performed for AOD2 dust, the results would be similar as for AOD1 dust after the fold-over series. The same involves also the EAF2 dust.

The most distinct interactions in Figure 27, that represents AOD1 dust, are between NaOH concentration and L/S ratio, and between bubbling gas and agitation speed. In dilute leach solution the amount of dust affected zinc dissolution, whereas the zinc extraction percent was not influenced by L/S ratio in strong 8 M NaOH solution. This interaction was also statistically significant for AOD1 dust according the Pareto chart (Figure 21). In the other interaction higher agitation speed increased zinc dissolution when oxygen gas bubbling was used, whereas with nitrogen gas bubbling stirring rate did not affect extracted zinc percent. Other interactions with these factors seemed to be rather marginal, indicated by nearly parallel lines.

In case of EAF1 dust the most distinct interactions were between L/S ratio and bubbling gas, and between NaOH concentration and bubbling gas. Bubbling with oxygen reduced zinc extraction with high amount of solid but enhanced it when the amount of solid was low. In Pareto chart this interaction was slightly over the statistically significance limit.

The other interaction was only at limits of significance. In strong NaOH solution nitrogen gas bubbling increased zinc extraction percent whereas in a weak solution gas bubbling had smaller but opposite effect.

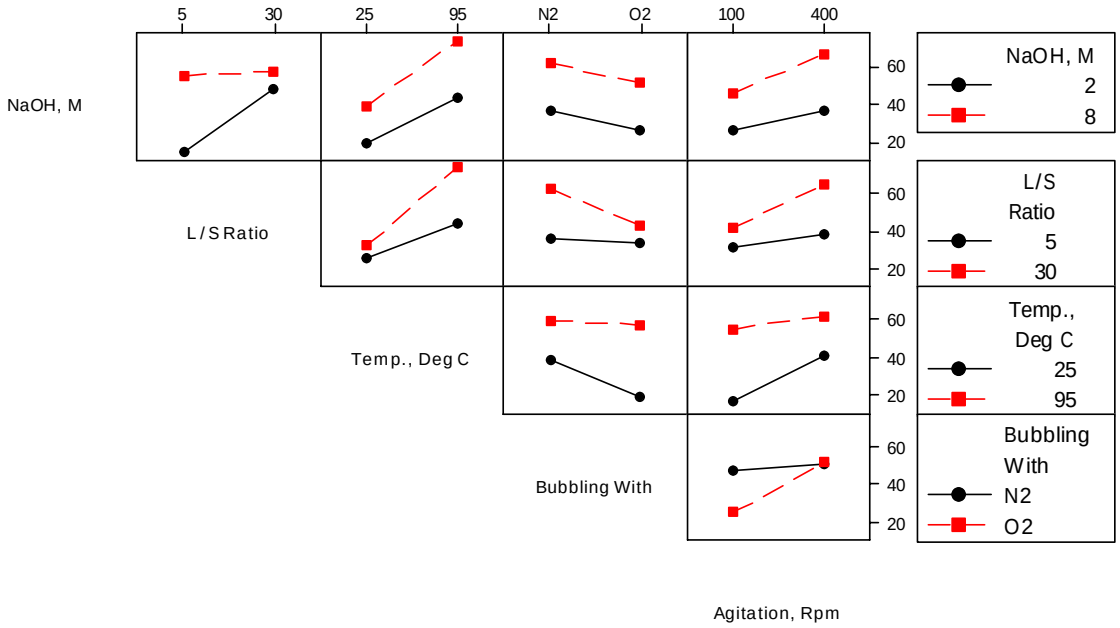


Figure 27. Interaction chart for AOD1 dust from the results of 2^{5-2} and fold-over designs.

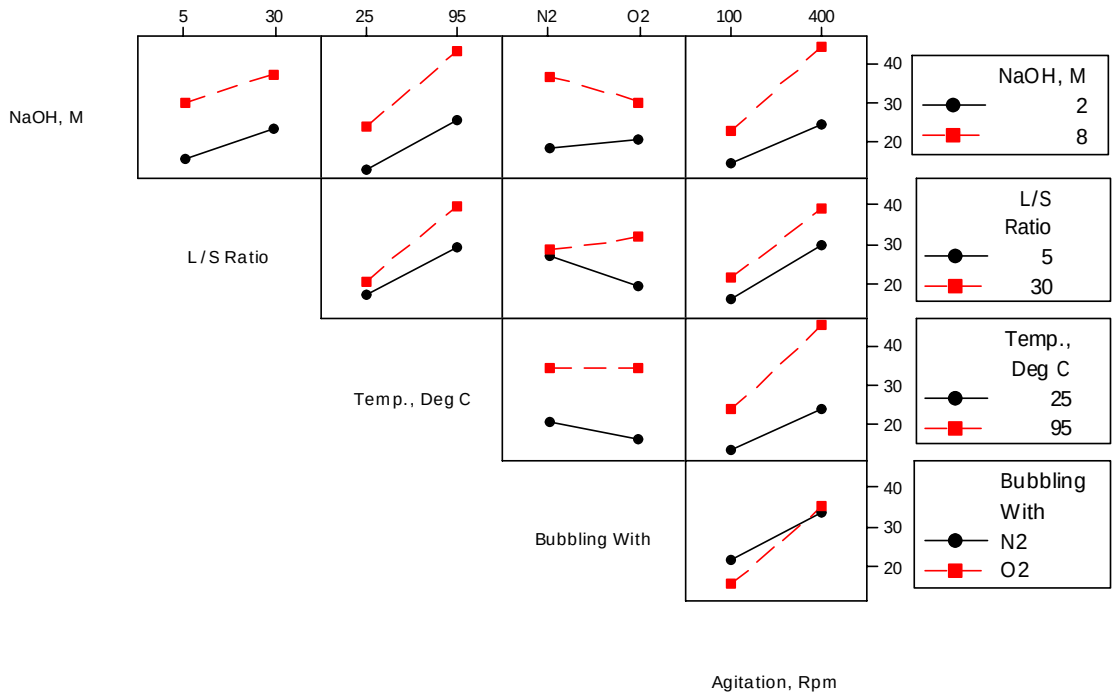


Figure 28. Interaction chart for EAF1 dust from the results of 2^{5-2} and fold-over designs.

An explanation for the most obvious interactions found from the charts after fold-over series is hard to conclude. The interactions that came up when only 2^{5-2} design were performed were mostly between NaOH concentration, temperature and agitation [III,IV]. Those can be explained with the high viscosity of strong NaOH solution. High temperature decreases viscosity and thus the need of strong agitation.

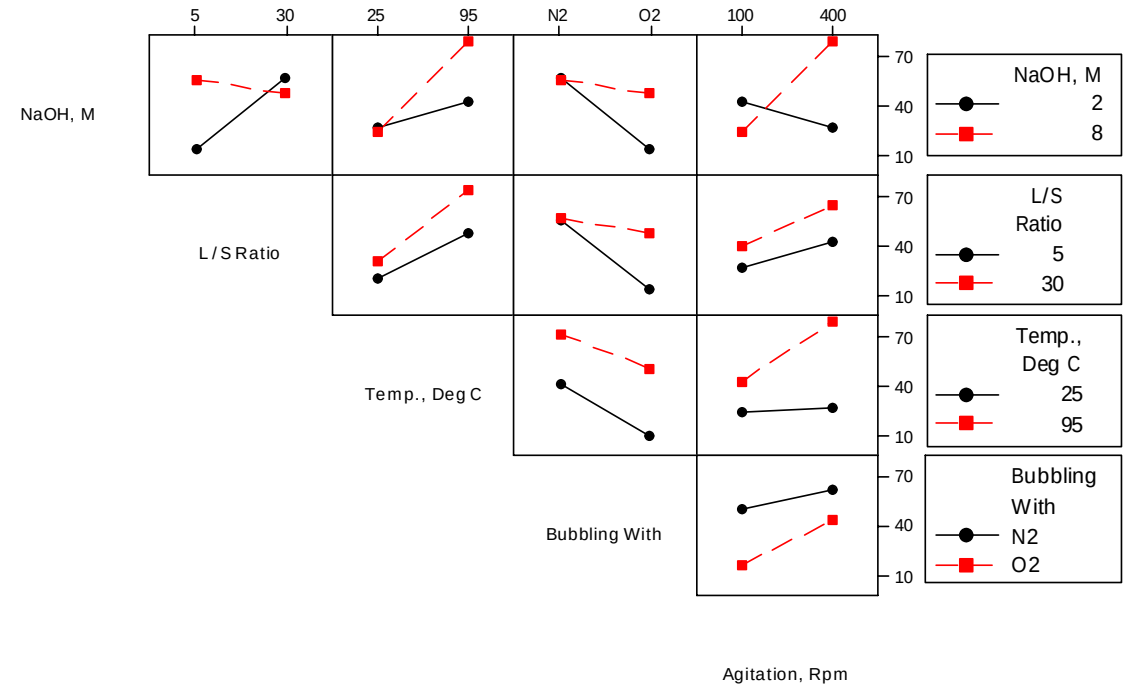


Figure 29. Interaction chart for AOD1 dust from the results of 2^{5-2} design.

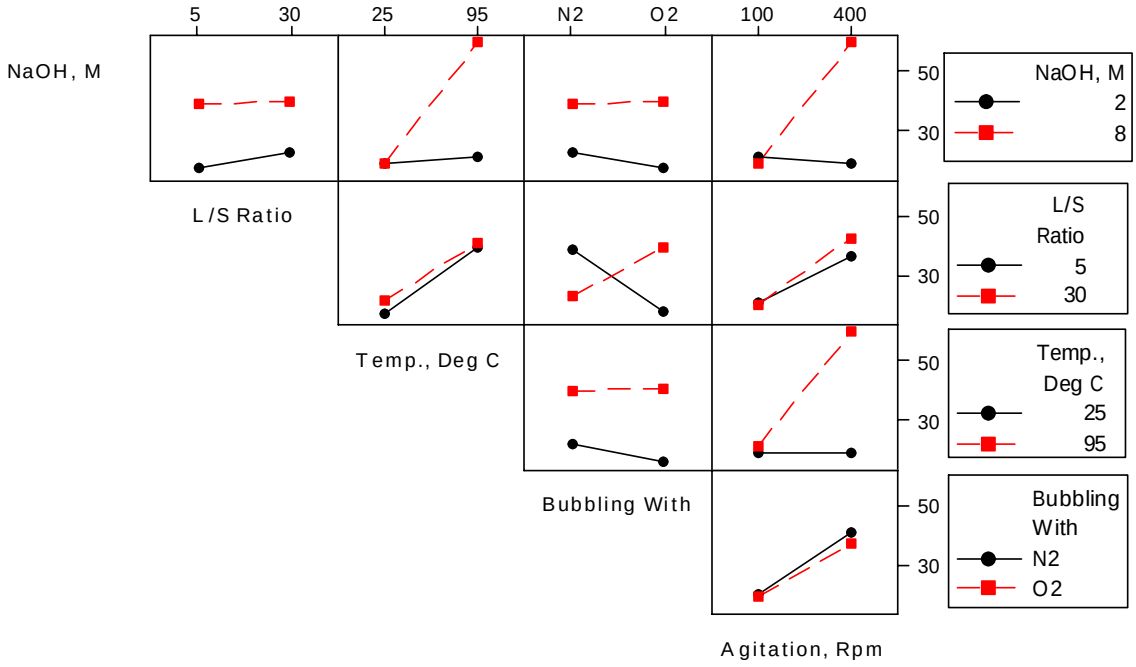


Figure 30. Interaction chart for EAF1 dust from the results of 2^{5-2} design [IV].

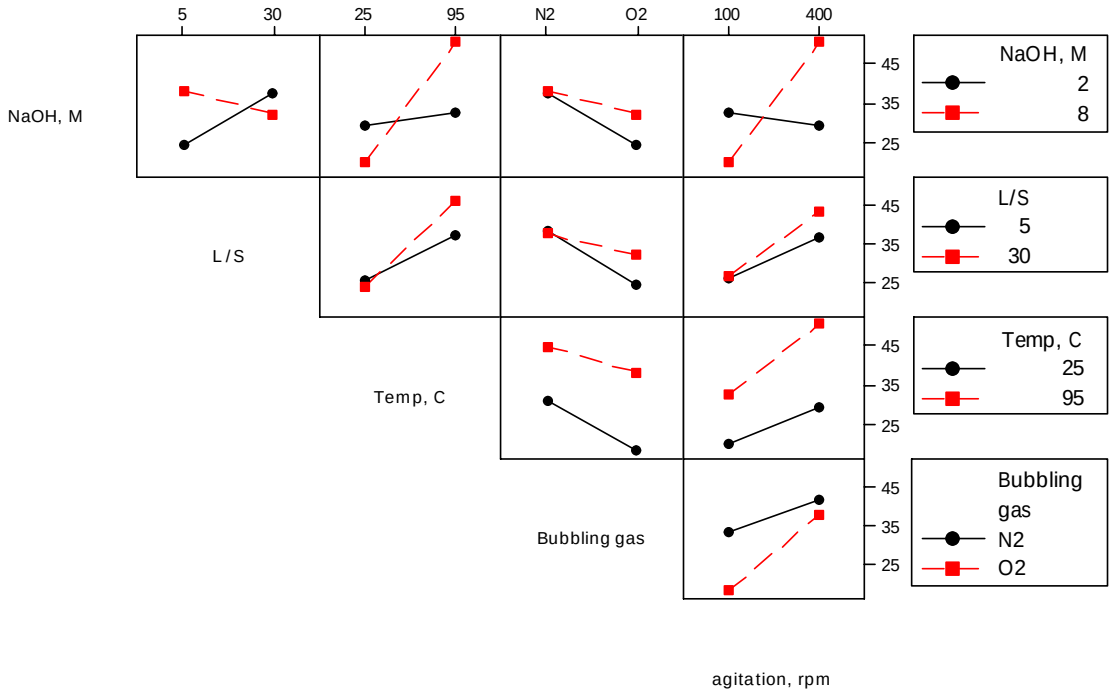


Figure 31. Interaction chart for AOD2 dust from the results of 2^{5-2} design.

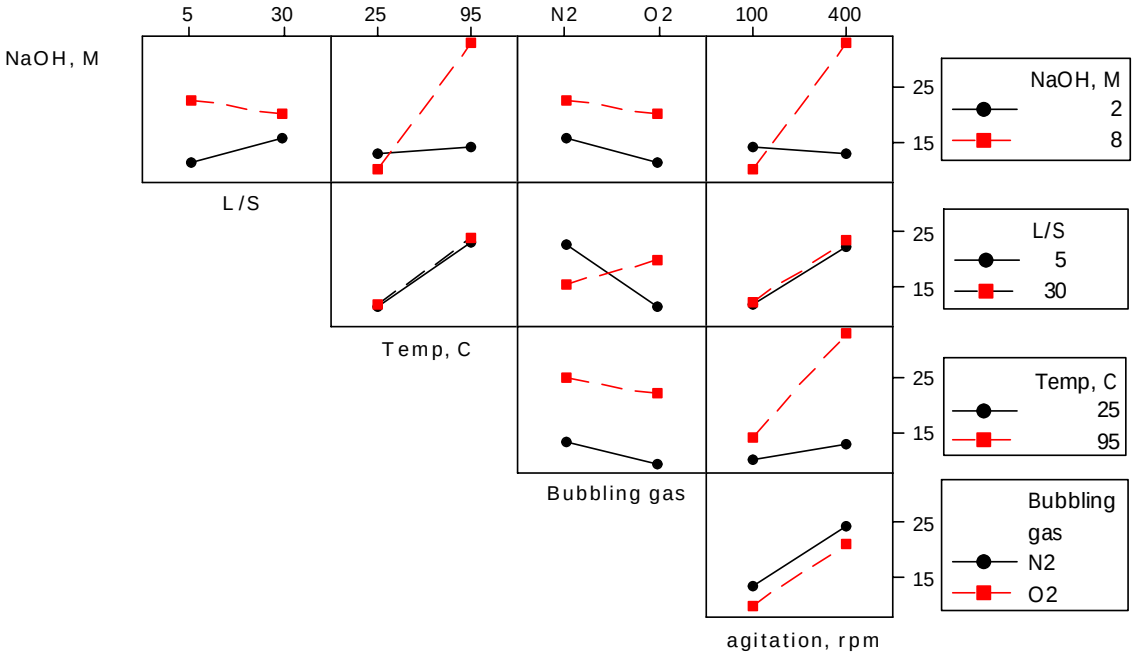


Figure 32. Interaction chart for EAF2 dust from the results of 2^{5-2} design [IV].

5.3 Dissolution of other elements

The results for the samples after 120 min leaching that were analyzed with ICP-EAS are presented in Table 7. The results showed that zinc was leached selectively and alloying elements are not leached substantially. Practically no iron (< 1.5 – 16 mg/l) or nickel (< 0.1 – 0.21 mg/l) was dissolved [I-IV]. Also the tests with ammonium thiocyanate (NH_4SCN) indicator showed that iron did not dissolve [I]. The leaching conditions had only minor effect on dissolution of chromium and less than 4 % of chromium was leached at most from all the studied dusts. In some samples from the EAF2 dust the amount of lead and cadmium was a bit higher, however, only 9 % of lead and 1 % of cadmium was leached [IV].

Table 7. Amount of most important elements in leachate after 120 min leaching.

	Amount in leachate (mg/l)			
	AOD1	AOD2	EAF1	EAF2
Zn	394 – 14950	194 – 3722	169 – 8690	145 – 3234
Fe	< 1.5	< 1.5	< 1.5	< 1.5 – 16
Cr	27 – 484	< 1 – 258	43 – 277	47 – 446
Ni	< 0.1	< 0.1 – 0.11	< 0.1 – 0.21	≤ 0.11
Mo	3 – 56	193 – 2834	4 – 32	18 – 263
Ca	< 5 – 21	< 5 – 10	< 5 – 7	< 5 – 14
Pb	< 2.5 – 24	< 2.5 – 61	3 – 62	< 2.5 – 188
Cd	< 0.25	< 0.25	< 0.25	< 0.25 – 6.51

In Figure 33 is shown the amount of the main elements in the leach samples from the experiments at the two leaching conditions that gave the highest zinc extractions. These histograms also verifies that leaching with strong and hot caustic soda solution produces a zinc containing solution with only minor amounts of other elements. In addition to zinc, molybdenum dissolved well (67 – 100 %) and its amount (mg/l) was almost the same than zinc in the leachates from AOD2 dust, in couple samples it was even slightly higher [III]. Also from EAF2 dust Mo was leached a bit more [IV]. However, the amount of Mo

was low in the other dusts compared to AOD2 dust thus also its amount (mg/l) was low in relation zinc in the leachates.

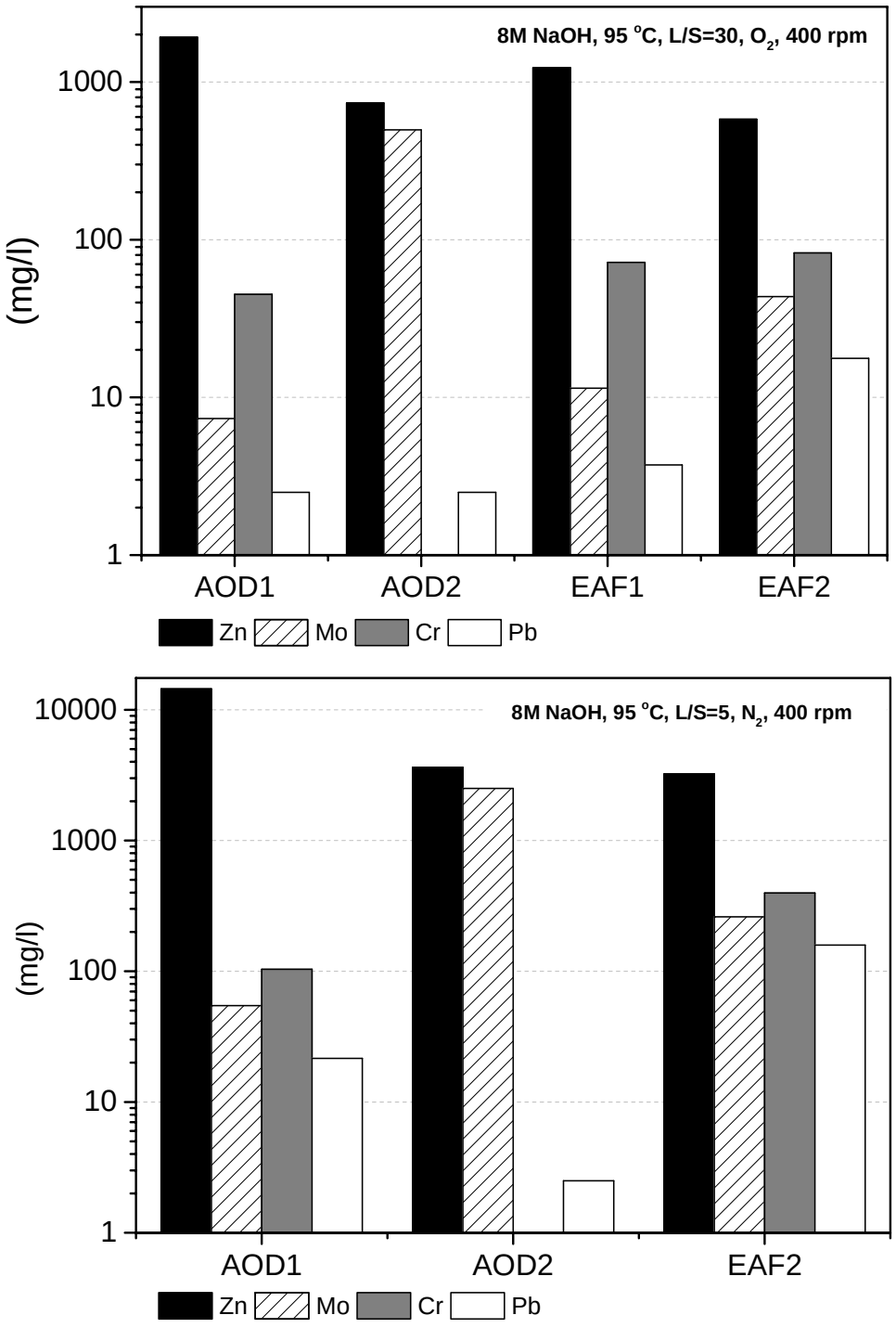


Figure 33. The extraction of zinc, molybdenum, chromium and lead in strong and hot NaOH solution.

6 DISCUSSION

The results showed that 80 % of zinc was dissolved at the most from the AOD1 dust and the maximum was less for the other dusts. Difference in maximum zinc extraction between the dusts arose most likely from the mineralogical differences of the dusts and is depended on the amount of zinc in ferrite form. Dissolution of synthetic zinc ferrite in NaOH solutions has been reported to be low (max. 9%) [47] whereas pure zinc oxide has seen to dissolve completely and very rapidly in strong NaOH solution [48]. Hereby, the leaching results verify that part of zinc occurs in insoluble ferrite form and part in soluble zincite.

Only a qualitative mineralogical analysis could be determined for the dusts and both zincite and zinc ferrite were identified in all dusts [44]. After the leaching experiments it can be stated that in the dusts of which low maximum recoveries were achieved larger part of zinc was in ferrite form. The soluble zincite accounts for around 80 % of zinc in AOD1 dust, around 50 % in AOD2 dust, around 60 % in EAF1 dust and around 30 % in EAF2 dust. In carbon steel making dusts 30 – 70 % of contained zinc is reported to be in ferrite form and lower Zn/Fe molar ratio increases ferrite share [23]. It is also possible that part of zinc occurred in glass inclusions or encapsulated inside of other phases and thus was not leached. The studied stainless steel dusts contained considerable amounts calcium oxide that has showed to inhibit the dissolution of glassy SiO_2 in 5 M NaOH solution [49].

It was observed from the shape of the leaching curves that the dissolution of zinc is fast, in both high and low recoveries of zinc. A large part of leachable zinc is dissolved in few minutes and after that extraction increased only slightly. This behavior indicates that for the process the time dependence is rather negligible after 30 – 60 minutes. Fast dissolution of zinc from the dust has also been reported in previous studies with carbon steel flue dusts [19, 33]. Usually, the maximum recovery was achieved at the end of the test (120 min). However, in some experiments the maximum yield of zinc was achieved earlier and then it decreased, which may indicate that part of zinc was precipitated back.

The leaching conditions affected the amount of extracted zinc and elevated NaOH concentration, temperature, agitation speed and L/S ratio, and nitrogen gas bubbling had

improving effect on zinc dissolution. The dust from same furnace type behaved similarly, for AOD dusts all studied leaching factors were statistically significant whereas for EAF1 dust gas bubbling and for EAF2 dust L/S ratio were found to be statistically insignificant. The original plan was to control redox potential by oxygen or nitrogen gas bubbling in order to measure the actual redox potential and to study its effect as a one factor on zinc dissolution (among the NaOH concentration, temperature etc.). However, measuring the redox potential was found to be impossible with the available electrodes in the leaching experiments and therefore instead of the quantitative potential value the qualitative gas composition was chosen as a factor. No previous data was found on the influence of redox potential or gas bubbling for the leaching of steelmaking dusts. The dissolution was found not to follow electrochemical mechanism but chemical mechanism. Therefore the higher redox potential supposed to improve leaching had no beneficial effect.

The most important factors seemed to be NaOH concentration, temperature and agitation speed, an increase of those three factors improved the zinc extraction predominantly. These are consistent with the chemical dissolution mechanism with partially reaction rate and partially mass transfer control. The caustic soda leaching studies with carbon steel flue dusts have also showed that hot and strong NaOH solution is needed in order to reach higher levels of zinc dissolution [1, 19, 40]. The disadvantage with strongly concentrated NaOH solution is that filtration is difficult due to the high viscosity of strong NaOH solution and extremely fine-grained dust. It was seen during the experiments that handling the dusts was rather difficult and especially EAF1 dust was very sticky. This may cause problems when considering to scale up the leaching of dust into industrial applications. The other disadvantages with hot and strong NaOH solutions are that NaOH is also quite expensive reagent and heating increases the energy cost.

As concentration, temperature and agitation speed were proven to be influential for all dusts, the reaction control mechanism is difficult to conclude. If the reaction rate is affected by stirring, it could indicate that the reaction is diffusion controlled under those conditions. On the other hand, increasing temperature had improving effect that indicates reaction to be chemically controlled. Increasing temperature is much less significant for diffusion-controlled reactions/processes than for a chemically controlled. [37]

The found two-factor interactions were similar for the dusts from same furnace type after the 2^{5-2} fractional factorial experiments but when the fold-over experiments were also performed less two-factor interactions were found between the factors. The 2^{5-2} fractional factorial design is a resolution III design when the main effects are confounded with two-factor interactions and the full fold-over design eliminated those confoundings and increased the ability to separate the main effects and interactions from one another. Gas was a participating factor in most of the most obvious two-factor interactions found from the charts of fold-over experiments and for these interactions an explanation is hard to conclude.

The coefficients of the regression equation factors describing zinc dissolution from different dusts are shown in Table 8. The coefficients are given by the Minitab software and only the statistically significant main factors and second level interactions are shown. Because the equations sum up the effect of several factors on zinc extraction, the trend of an individual factor in the equation may not be same that shown in the main effect plots. The regression equations can be used for calculation of predicted value of zinc extraction % in the way shown below:

$$Y(AOD1) = -10.313 + 0.101C + 5.171A + 0.458B - 0.209AB...$$

Y is the predicted value of zinc extraction (%) from the AOD1 dust and A, B and C are uncoded (transformed to dimensionless with range of +/-1 in determining the regression equation) factors.

The experiments showed that zinc was dissolved selectively from the dusts and practically no iron, nickel and chromium were dissolved. This selectivity has considered the major benefit of caustic soda leaching. Earlier studies of caustic soda leaching of dusts from iron and steel mills have also showed good selectivity in dissolving zinc compared to iron compounds [1, 19, 28]. As iron and the valuable alloying elements such as chromium and nickel remained in the leach residue, they could be recovered by recycling the residue back to melting if the amount of zinc can be lowered to a sufficient level. The main problem to be solved is that the dissolution of zinc is limited due to the presence of zinc ferrites. However, for breaking down zinc ferrites an additional pre-treatment such as roasting might be used. For example caustic soda roasting prior to

leaching has showed to improve greatly zinc dissolution from unalloyed EAF dusts in alkaline solutions [11, 29].

Table 8. Coefficients of the studied leaching factors.

Factor		**AOD1**	**AOD2**	**EAF1**	**EAF2**
Constant		- 10.313	10.944	2.163	- 8.151
NaOH (M)	= A	5.171	0.700	- 0.165	1.301
L/S (l/mg)	= B	0.458	- 0.415	- 0.101	
Temp. (ºC)	= C	0.101	0.133	0.077	0.167
Gas (N_2/O_2)	= D	0.877	- 4.836		- 1.690
Stirring (rpm)	= E	- 0.016	0.032	0.012	0.034
NaOH*L/S		- 0.209			
L/S*Temp.		0.013	0.006		
L/S*Gas		- 0.347		0.217	
L/S*Stirring		0.002	0.001		
NaOH*Stirring		0.006		0.006	
NaOH*Gas				- 0.702	

It would be also a great benefit if zinc can be recovered from leach solution. By hydrometallurgical processes can be produced a virgin quality of non-ferrous metals [38]. Electrowinning is the most important method in producing zinc and around 80 % of produced zinc in the world is obtained by this technology [11]. This technology usually uses acidic sulfate solution but a sponge-like, particulate zinc deposit can be produced in caustic soda solution [38].

In order to produce pure metals from the leach solution, the solution should contain very few impurities. Especially dissolved iron causes problems in recovering metals from the leach solutions that has been the major drawback with acids. From NaOH leach solutions lead, cadmium and copper can be removed from the leach solution by cementation with zinc powder [27]. After solution purification zinc can be recovered as solid zinc by electrolysis or precipitated as its pure compound. By NaOH leaching stainless steel flue dusts a relative clean and iron-free solution was obtained and the concentrations of other elements in relation to zinc are low in leachate solution in which case the leach solution might be suitable for recovering zinc.

7 CONCLUSIONS

The disposal and re-use of dusts formed in stainless steel production has been a serious concern for the industry as in most industrial countries stainless steel dusts are considered as hazardous waste. At the same time these dusts are also source of valuable metals but the extraction and recovery of the valuables is difficult due their complex composition. The most troublesome element in the dust is zinc, which vaporizes easily and condenses into steel production fumes ending up in the flue dust or sludge usually as an oxide or ferrite. In this study different flue dusts from stainless steel production were leached in NaOH solutions in order to remove zinc. The studied dust samples included argon-oxygen decarburization (AOD1 and AOD2) converter dusts and electric arc furnace (EAF1 and EAF2) dusts from the two production lines of Outokumpu Stainless Tornio Works.

The main objectives of this study were to selectively leach zinc out from the dusts so that the remaining (Ni, Cr, Fe) oxide material could be recycled back to melting and to find the effect of various leaching factors on zinc dissolution. The results from factorial tests showed that the leaching conditions affected the amount of extracted zinc and that elevated NaOH concentration, temperature, agitation speed and L/S ratio, and nitrogen gas bubbling had improving effect on dissolution. The dust from same furnace type behaved similarly, for AOD dusts all studied leaching factors were statistically significant whereas for EAF1 dust gas bubbling and for EAF2 dust L/S ratio were found to be statistically insignificant. The two-factor interactions were not that easy to observe and bubbling gas was a participating factor in most of the most obvious two-factor interactions found from the charts of fold-over experiments. For these interactions an explanation is hard to conclude.

An increase in the NaOH concentration, temperature and agitation improved the zinc extraction and there were two leaching conditions in the test series in which zinc extraction was greatest for all four dusts. In both, strong 8 M NaOH solution with high temperature and stirring rate was used, but the bubbling gas and liquid to solid ratio changed. Almost equivalent zinc extraction achieved in these two leaching conditions and was around 80 % for AOD1 dust, around 50 % for AOD2 dust, around 60 % for the

EAF1 dust and around 30 % for the EAF2 dust. Difference in zinc extraction between the dusts arose from the mineralogical differences and is dependent on the amount of zinc in ferrite form. In all dusts zinc occurred both as easily soluble zinc oxide and as poorly-soluble ferrite form.

This study showed that alkaline leaching of zinc from stainless steel AOD and EAF dusts using NaOH solutions is selective and practically no iron, chromium and nickel were dissolved. However, the dissolution of zinc is limited due to the presence of zinc ferrites and that remains the main problem to be solved. When considering the possibility to recycle dust back to the process, the amount of zinc should be low to effectively recycle dust back to the process. The leaching process can work in zinc removal if zinc ferrites are decomposed prior to leaching, for example by roasting.

I would also be reasonable to do further experiments at the center point that can be added to the factorial designs used in this study. After that the response of surfaces can be defined and the possible curvature of the process would come up. Then the leaching conditions can be optimized for the best zinc extraction from the dusts. For optimizing the most reasonable leaching conditions also the cost of heating and the price of NaOH are important factors.

8 REFERENCES

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Effect of Leaching Parameters on Zinc Removal from Stainless Steel Dusts

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Abstract

Stainless steel production generates significant quantities of dusts and sludge, which are classified as harmful waste making it expensive to use them as landfill. In addition, direct recycling of dust back to stainless steel production is hindered due to the presence of zinc in the dust. Today these dusts are recycled in separate treatment plants. However, there are still significant problems associated with treating this material and the developed pyro-, hydrometallurgical and combined processes have not been entirely satisfying.

Metal extraction from the dusts is difficult due to their complex composition and finding a suitable process is complicated as each dust is unique. The major obstruction in the hydrometallurgical extraction of zinc is the presence of zinc ferrite ($ZnFe_2O_4$), which is very stable compound. Among hydrometallurgical methods the advantage in alkaline leaching is the selective solubility of zinc and obtaining relatively clean iron oxide solids.

In this work stainless steel converter dust, from Outokumpu Stainless (Tornio, Finland), was leached using NaOH solutions. The focus was to determine the optimum leaching conditions for zinc removal. The dust samples were leached under atmospheric pressure and the variables tested were temperature, sodium hydroxide concentration, liquid to solid ratio (L/S), redox potential, and stirring rate. All the studied variables had effect on leachability of zinc and only redox potential had a negative response. The interactions were not easy to observe. The dissolution of zinc was fast and zinc was leached selectively with caustic soda. Iron did not dissolve and only minor parts of the alloying elements were leached and relatively clean zinc solution was obtained.

1 Introduction

Stainless steel production generates significant quantities of various solid wastes in form of dusts and sludges, and the amounts of these wastes are increasing. Their disposal or possible re-use has been a

serious concern for the industry. In most industrial countries stainless steel dusts are considered as harmful waste as they contain a significant amount of toxic elements such as heavy metals. Thus, they must be must be stored in specialized landfill areas, which increases the costs of disposal.

On the other hand, stainless steel dusts contain valuable metals such as chromium, nickel and zinc, which can be recovered and reused in a judicious manner. Recovering them will save raw material costs and reduces environmental impact as the disposal of these dusts has become expensive due to harmful elements. In case of disposal the valuable metals are lost. From economic and environmental point of view it is desirable to recover the valuables and utilize these wastes [1]. Direct recycling of dust back to stainless steel production is not possible because they contain considerable amounts of elements that cause operational difficulties in the steel making process [2]. The use of scrap as a raw material in electric arc furnaces (EAF) and converters brings other elements to the dusts. The element that causes the most problems in treating flue dusts is zinc, which vaporizes easily and condenses to steel production fumes ending up in the flue dust or sludge usually as an oxide or ferrite.

Because some of these dusts are not possible to recycle directly or be used as landfill, it is necessary to consider the recovery of valuable elements from them and to obtain residue that can be reused or safely disposed-off without affecting the environment [2]. There has been an increasing interest in developing processes for the recovery of zinc from the dusts. A number of pyrometallurgical, hydrometallurgical and combined processes have been developed to allow better utilization of steel making dusts in primary operations [3, 4]. There are still significant problems associated with treating this material and none of the developed processes have been entirely satisfying [5].

Today the dust treatment processes are predominantly pyrometallurgical and dusts are recycled in separate treatment plants. The drawbacks with pyrometallurgical processes are high energy consumption and a need of gas cleaning system. Moreover, they require relatively large tonnage of dust to be economically competitive. Thus, there is an impetus for developing hydrometallurgical processes as a small-scale, on-site process could be economical because of the low capital operating cost as well as the potential recovery of the valuable metal-containing products. Hydrometallurgical processes on a small scale are regarded as more environmentally suitable and economical for treating materials having relatively low zinc content. Several hydrometallurgical methods for the recovery of zinc and other metals from these zinc-bearing wastes have been proposed. Usually the basic process scheme has been leaching, solvent extraction and electrowinning. Some of these have been commercialized for some time and then abandoned. Most of these processes are still at an experimental stage [5-7].

Dusts containing many elements make metal extraction complex and difficult. In addition, each dust is unique which makes finding a suitable treatment process even more complicated. The major obstruction in the hydrometallurgical extraction of zinc is the presence of zinc ferrite ($ZnFe_2O_4$) in the dust which is a highly stable compound.

Usually, the most important stage is the separation of the iron from non-ferrous metals such as zinc, lead and cadmium. Leaching of steel making dusts can be done with acids or bases. Previous

researches have concentrated on the leaching of carbon steel dusts, and for this purpose both acid and base leaching based laboratory and pilot set-ups have been constructed. Among the hydrometallurgical methods, the advantage in alkaline leaching is the selective solubility of zinc compared to iron compounds and thus relatively clean and iron-free solution is obtained and the complicated iron removal processes is avoided.

The focus in this study has been on the treatment of stainless steel converter dust from Outokumpu Stainless (Tornio, Finland) by an alkaline leaching in order to determine optimum leaching conditions for zinc removal. The effect of temperature, sodium hydroxide concentration, liquid to solid ratio (L/S), redox potential and stirring rate were tested. The target is to leach zinc out of stainless steel making dusts as fast and as much as possible. Another goal is to minimize the zinc content in dust, aiming at < 0.1 % Zn in dust residue. This would provide an opportunity to effectively recycle the dust back to steel making process. Alkaline leaching was chosen as it is effective in the dissolution of zinc while leaving the iron in the solid residue.

2 Dust formation in stainless steel industry

In stainless steel production dusts are generated in chrome converters, electric arc furnaces (EAF), and argon oxygen decarburization converters (AOD). The stainless steel process chain begins in a chrome mine and goes through a ferrochrome and a steel plant until the rolling processes (Figure 1). In a chrome converter the silicon and part of the carbon is removed with oxygen blowing. Stainless steel is produced by preparing a chromium-containing steel melt in an electric furnace and subsequently by decarburizing in an argon–oxygen–decarburization (AOD) converter. From the converters the melt is moved with ladles in which the final composition is set [8]. During the production of stainless steel iron, between 30 and 70 kg of dust and fine waste is generated per ton of steel [9].

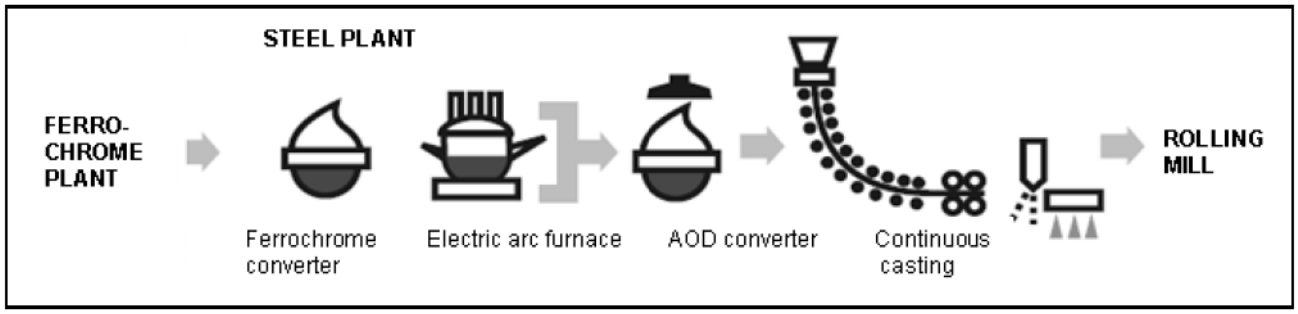

Figure 1: Stainless steel production chain from ferrochrome plant to rolling mill [8]

Dust and sludge produced in ferrochrome and stainless steel plants contain significant amount of chromium. Chromium is a toxic element which can leach into the groundwater when stockpiled or landfilled and thus these dusts must first be treated. In addition, dusts contain other valuable components such as nickel and zinc [10, 11].

The chemical compositions of, and crystalline phases present in the dusts vary considerably depending on the steel grade produced, raw materials used, operation conditions and procedures. Typically dusts generated in stainless steel making are relatively low in lead and zinc, but richer in alloying

elements, such as chromium, nickel, manganese, etc. [6]. Stainless steel dust consists mainly of oxide phases that are rich in Fe, Cr, Ca, Zn, Mg, Mn and Ni, with minor amounts of phases that contain alkaline metals (K, Na), halogens (Cl, F), Si, Mo, Pb and S [10]. Fe in dust is most prevalent in Fe_3O_4 phase, 50 to 80 % of zinc is present as ZnO, rest balanced mainly as compound with Fe in a mixed zinc-iron ferrites spinel [12]. The amount of ZnO (zincite) varies with the percent zinc present in the sample, and increases with the zinc content [6, 10]. The choice between the processing routes depends strongly on the dust characteristic. Therefore a detailed dust characterization is important for defining the most appropriate leaching strategy.

The dusts studied in this work are from (Outokumpu) stainless steel plant, from the AOD1 converter. Majority of stainless steel produced in Tornio are standard austenitic grades containing nickel in addition to chromium and iron, but also produces ferritic stainless steels [13]. The capacity of Outokumpu's steel smelter is 1.7 million tons of casted billets per annum [8]. About 3 wt. % of the total dust of stainless steelmaking forms through vaporization in the AOD converter, while the ejection of metal and slag by the bursting of gas bubbles is the main dust forming mechanism (about 91 wt. % of the total) [10].

3 Alkaline leaching of zinc from steel making dusts

Hydrometallurgical processes are considered to be suitable for such an on-site treatment [14] and they offer an interesting alternative for zinc recycling if iron dissolution can be controlled [15, 16]. In hydrometallurgical processes metals are extracted by a leaching stage and then recovered, for example in metallic form by electrolysis [17]. In the leaching stage selective solubility of zinc relative to iron compound is critical.

Among the hydrometallurgical processes alkaline leaching has the advantage that iron does not dissolve compared to acidic leaching. A relatively clean and iron-free leach solution can be achieved by alkaline leaching and the very complicated iron removal process is avoided. Also the high alkalinity of many dusts makes their acid leaching expensive, because they consume a lot of acid for pH adjustment [2, 18]. Therefore NaOH leaching could be a promising leaching method and sodium hydroxide is one of the common bases used for leaching amphoteric hydroxides or oxides [19].

The individual particles in the dust are mostly less than 10 µm and difficult to handle dry, if no previous agglomeration is used [15]. In addition, the reaction kinetics involving this dust should be fast, which suggest that leaching may be an attractive route to treat this kind of material [12, 15]. The most important parameters controlling the efficiency of the leaching process are oxidation potential, concentration of leaching agent, temperature, and pH. Principal factors increasing leaching rate are [19]:

1. Decreasing particle size.
2. Increasing the speed of agitation, if the leaching process is diffusion controlled (chemically controlled processes are not influenced).
3. Increasing temperature (less significant for diffusion-controlled).
4. Increasing concentration of the leaching agent (optimum level to maximize selectivity).
5. Decreasing pulp density (small volume of solids).

If an insoluble reaction product is formed on the particles during leaching, the dissolution rate depends on the nature of this product [19].

Alkaline leaching, using sodium hydroxide as a leaching agent is seen effective in the dissolution of heavy metals, without significant dissolution of iron [15]. Oxides of Zn, Pb and Al dissolve effectively with a strong NaOH solution and in some cases Cr and Cu can be dissolved. Thus, the consumption of leaching agent decreases and a solution containing Zn and Pb as predominant elements will be obtained. The earlier experiments have shown that the solubility of these amphoteric elements in strong alkaline solution decreases in the following sequences [7].

Zn > Pb > Al > Cr(III) > Cu

The solubility of Cr(III), Cu and Cd are found to be negligible. If iron is dissolved it can be oxidized and precipitated by aeration [20]. Considering these, it would be appropriate to use the alkaline processes to leach zinc and lead selectively from the dusts [7].

Only few processes developed for treating dust and to recover the valuables have reached commercialization. The major problem with hydrometallurgical treatment of dusts is the presence of zinc ferrite in the dust. Zinc occurs predominantly in two phases: Zincite (ZnO) and zinc ferrite ($ZnFe_2O_4$). From these zincite dissolves easily in many solvents, but zinc ferrite is difficult to decompose, both in acidic and alkaline solutions [21]. Around 50 to 80 % of zinc is present as ZnO, rest balanced mainly as compound with Fe in a mixed zinc-iron ferrites spinel [12]. The ratio of these phases of zinc depends on the type of furnaces and operations, especially the dust collection systems [14]. Total zinc recovery is limited by the amount of zinc present as zinc ferrite. Experiments have indicated that the maximum percentage of decomposed zinc ferrite has been only about 9 %. A pyrometallurgical roasting step can be used to convert zinc ferrite into soluble zinc oxide to maximize zinc recovery [5].

The main leaching reactions (1) and (2) in caustic soda leach can be expressed as follows [3, 22]:

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O \quad (1)$$

$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O \quad (2)$$

The dissolved lead can be recovered by cementation with zinc powder and after purification zinc can be recovered from the solution. Eacott *et al.* have conducted a technical and economical

profitability study of the caustic-electrowinning process. They claimed that the process is flexible and can be applied to small, medium or large-scale operations and that it is relatively clean in terms of work-place and ambient air emissions [22]. The drawback is that the solid-liquid separation is difficult with viscous NaOH solutions and due to the extremely fine-grained solid. However, it can be achieved with conventional equipment [3].

The alkaline leaching processes have been developed earlier and used for the leaching of zinc from the different oxidized ores and secondary materials. However, they have faced difficulties and have closed down. The U.S. Bureau of Mines investigated the recovery of zinc from the oxidized ores using NaOH in the 1960's [3, 4]. The process has also been tested to secondary ones, such as to different EAF dusts [22, 23]. Some pilot plants have been built to test hydrometallurgical technologies in alkaline leaching, such as Cebedeau and Cardiff processes. The Cebedeau process consisted of leaching in hot (95 °C) concentrated (6 to 12 M) NaOH solution [23] and resulted in a commercial plant in France 1986. However, the plant was reported insufficient [3]. The Cardiff process consists of two staged leaching with intermediate reduction roasting for complete recovery of zinc and lead. A pilot scale plant did run for a number of years [3].

Despite that technical and economic problems have emerged, hydrometallurgical processes, such as caustic leaching, could offer some potential advantages for treating stainless steel dusts. The cost/profitability of the process will be highly dependent on the zinc content of the waste, and, of course, on the market value of the recovered zinc [20]. An important factor will be the costs imposed to landfill. Reduction of these by using dust treatment can be decisive to process economics.

4 Test materials and methods

4.1 Dust characterization

Stainless steel production dust samples were obtained from Outokumpu Tornio Works and dust was originated from argon oxygen decarburization (AOD) converter. The AOD 1 dust was analyzed in University of Oulu, Technical University of Kosice and Labtium Oy, Espoo.

The samples were submitted in a particle size analysis by laser diffraction [24] and by Scanning-foto-sedimentograf [25]. All particles measured in Kosice were under 47 µm [25] and particles measured in Oulu were under 4 µm [24]. The smallest particles were under 1 µm [24, 25].

The samples were also submitted to a chemical and mineralogical analysis using optical microscopy, scanning electron microscope (SEM), Electron probe micro-analyze (EPMA), optical microscopy [24], X-ray diffraction (XRD) [24, 25], Atomic absorption spectroscopy (AAS) [25], and Inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results from chemical analyses are presented in Tables 1, 2 and 3. The main components in the dusts are iron, zinc, chromium and calcium. All the analyses gave similar levels of zinc in dust, as seen in Table 4. The zinc content is around 9.762 % for AOD1.

Table 1: The chemical composition of the samples analyzed by University of Oulu [24]

AOD1	S	Zn	C	V	MgO	SiO_2	Al_2O_3	TiO_2	MnO	P_2O_5
	0.1	10.8	0.1	0.01	2.3	1.9	0.1	< 0.1	3.7	< 0.1
	CaO	Cr_2O_3	F	Fe_2O_3	PbO	NiO	MoO_2	Cr^{6+}	Na	K
	7.2	13.5	0.86	54.0	0.1	0.9	< 0.1	0.42	0.15	0.89

Table 2: Chemical analysis of samples – melting at 1000 °C and dissolution [25]

	Zn	Fe	Ni	Cr	Mn	Pb	Cd	Ca	LOI
AOD1	9.75	29.20	0.67	18.56	1.35	0.09	0.19	5.50	1.35

Table 3: Results by ICP-AES (Labtium)

	Fe	Cr	Ca	Zn	Ni	Mg	Mn	K
AOD1	35.65	6.65	4.945	9.65	0.6235	1.25	2.385	0.859

Table 4: Zn content [%] in dust samples

Sample	Košice1	Košice2	Oulu	Labtium1	Labtium2	Average	S.D.
AOD1	8.96	9.75	10.80	9.37	9.93	9.762	0.690

According to qualitative phase analysis the identified phases in AOD1 dust were chromite ($FeCr_2O_4$), magnesioferrite ($MgFe_2O_4$), magnetite (Fe_3O_4), zincite (ZnO), bunsenite (NiO), trevorite ($(NiFe)Fe_2O_4$), cryptohalite ($(NH_4)_2SiF_6$) maghemite (Fe_2O_3), and lime (CaO) [25]. An optical microscope picture of the AOD1 dust is represented in Figure 2. Larger particles consist of several phases and particles containing silicon and silicon ferrous phases, inner chromite and outer Cr-Fe oxide, magnesiochromite and glass, oxides of Cr_2O_3 and FeO and as well slag components were identified. Some phases were encapsulated inside of particles. Zinc was found to be present as zincite (ZnO) in AOD1 dust and occurs mainly in the fine fraction in which the maximum ZnO content is 14 % [24].

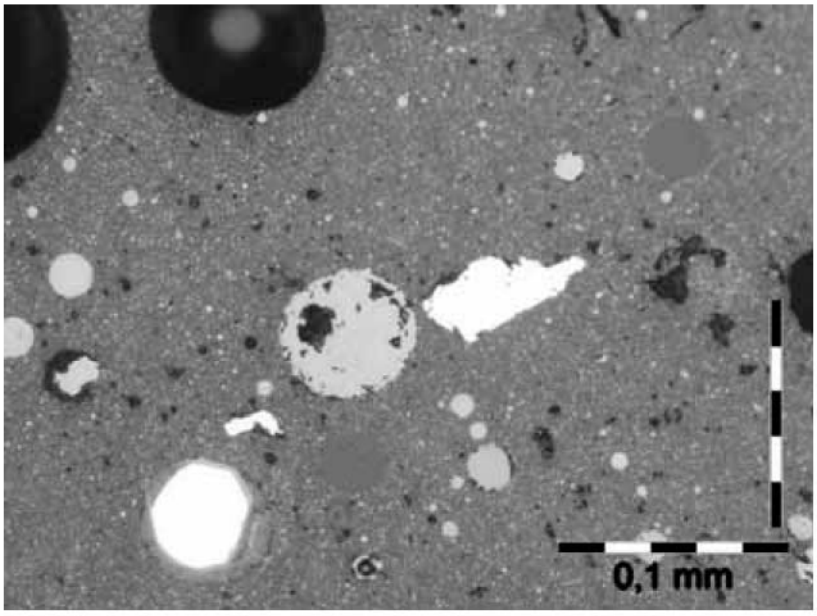

Figure 2: Optical microscopy picture of AOD1 dust sample [24]

4.2 Leaching experiments

The aim of the experiments was to investigate the leachability of zinc from the AOD stainless steel dust under different conditions and find the effects of leaching parameters. The leaching tests were carried out in the apparatus shown in Figure 3. The experimental setup for leaching test consisted of a thermobath (Lauda AquaLine AL25), glass cell and motor driver stirrer (VWR VOS16).

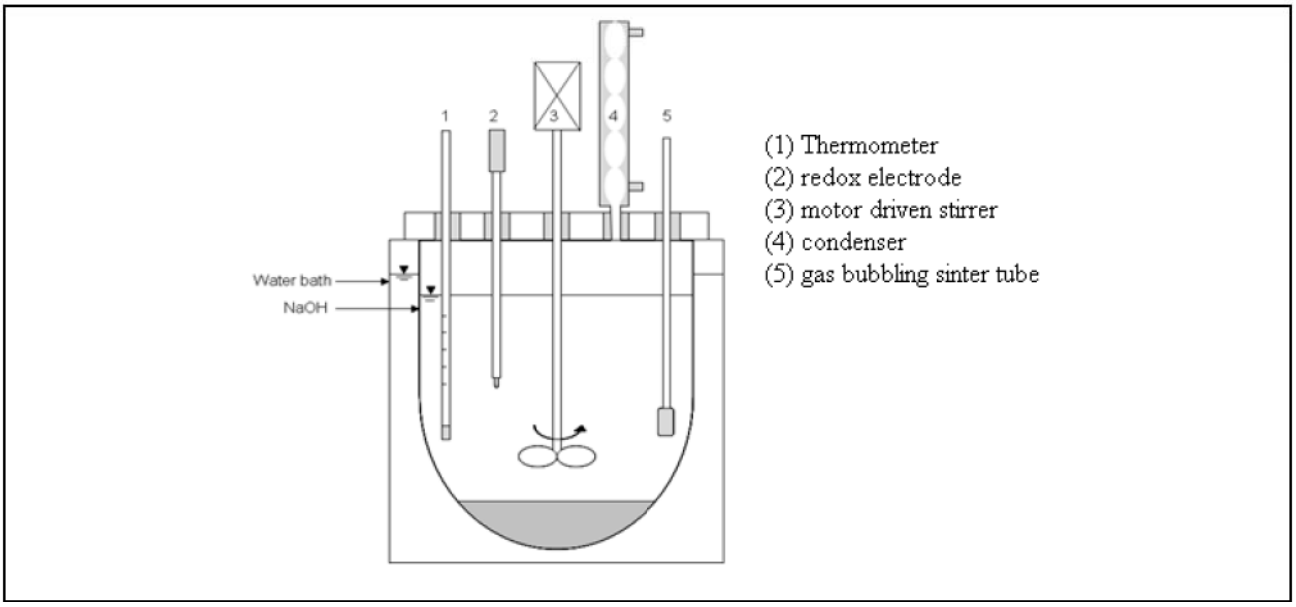

Figure 3: Dissolution cell in water bath

The effect of leaching time, NaOH concentration, temperature, stirring rate and L/S ratio on zinc extraction was investigated. Before starting the leaching the redox potential adjusted by bubbling of oxygen or nitrogen gas and stirring rate was adjusted to 100 or 400 rpm. The redox potential were measured after 1 hour bubbling (Radiometer MC3051PT Platinum ring Ag/AgCl electrode) and then dust was charged into cell were 800 ml of NaOH solution were set. The concentrations of 2 M and 8 M of NaOH were used. The chosen liquid/solid (L/S) ratios were 5 and 30. For this 160 g or 26.67 g of dust was added to the cell. The temperature was controlled with the water bath to 25 °C or 95 °C. Redox potential in the cell was measured again after the leaching experiment (120 min).

A liquid sample with volume of 10 ml was taken off in the chosen time intervals of 5, 10, 15, 20, 25, 30, 60 and 120 minutes. The stirring was stopped 30 seconds before each sampling. The samples were filtered and all liquid samples were analysed for Zn content with Perkin Elmer 372 AAS device. The assumed amount of zinc in the dust was calculated with the average value of zinc in dusts from the characterisation analysis (Table 4). Presence of iron was tested with ammonium thiocyanate (NH_4SCN) indicator which reacts with ferric salts forming a deep-red ferric thiocyanate complex. By default no iron should be leached by NaOH from the dust.

4.3 Design of Experiments

The experimental test series was planned as factorial tests for temperature, NaOH concentration, solid-liquid ratio, stirring rate and redox potential, i.e. a high and a low level were used (Table 5). In this method values of several variables are changed at the same time and the influence of each variable is then evaluated. Several parameters are changed at a time to find out the most important variables and the interactions and optimise the leaching conditions for further experiments [26].

Table 5: Variables used in experiments

Experiment No.	NaOH [M]	L/S Ratio	Temp. [°C]	Bubbling	Agitation [Rpm]
1	8	5	95	N_2	400
2	8	30	25	O_2	100
3	2	30	95	N_2	100
4	8	30	25	O_2	100
5	2	5	25	O_2	400
6	2	5	25	O_2	400
7	8	5	95	N_2	400
8	2	5	95	O_2	100
9	8	5	25	N_2	100
10	2	30	95	N_2	100
11	8	30	95	O_2	400
12	8	30	95	O_2	400
13	2	30	25	N_2	400
14	2	30	25	N_2	400
15	8	5	25	N_2	100
16	2	5	95	O_2	100

5 Results and discussion

The results of leaching experiments are shown in Figure 4 and 5. In Figure 4 zinc recoveries are represented at conditions in which zinc was leached well. Figure 5 represents leaching conditions in which poor recoveries of zinc were obtained. The general trends that can be observed are that the dissolution of zinc increased with increasing NaOH concentration and temperature and with lower liquid-solid ratio. The redox potential was adjusted with oxygen or nitrogen gas, and the recovery of zinc seems to be better when nitrogen gas is used. From the shape of the leaching curves in both Figures (4 and 5) can be observed that the dissolution of zinc is fast (in both high and low recoveries of zinc) and occurs in a few minutes.

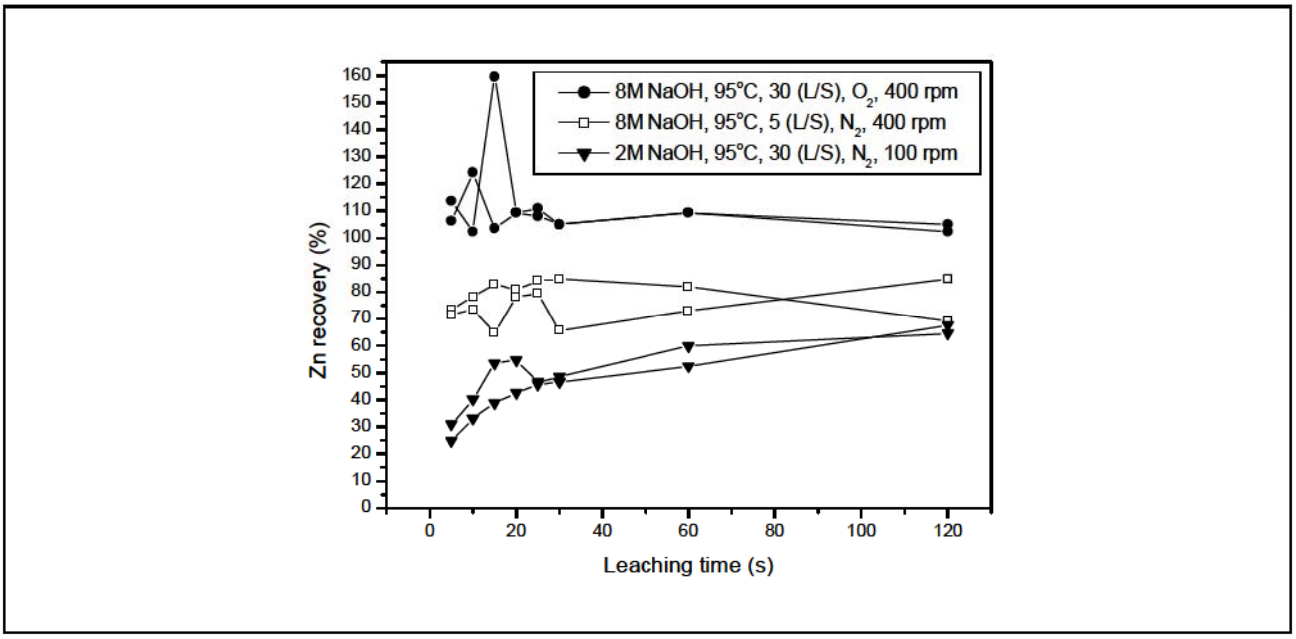

Figure 4: Recoveries of Zn in conditions that gives good yield

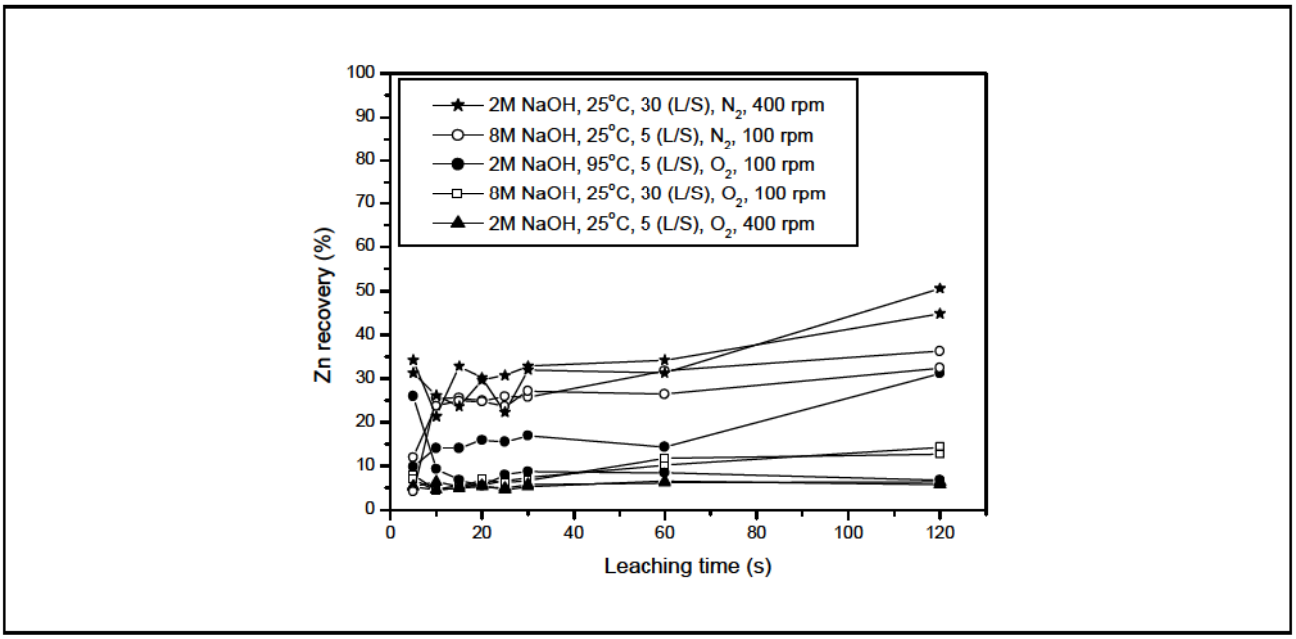

Figure 5: Recoveries of Zn in conditions that gives poorer Zn yield

Usually the maximum recovery was achieved at longest leaching time (120 min), however, in some conditions the maximum yield of zinc was achieved earlier and then it decreased, which may indicate that part of zinc was precipitated back.

In Figure 4, in which the zinc recoveries were greatest, in all leaching experiments high temperature of 95 °C was used. The maximum values of extracted Zn around 100 % was obtained leaching by using 8 M NaOH solution and strirring rate of 400 rpm at the temperature of 95 °C. The liquid-solid ratio was 30 and oxygen bubbling was used.

Figure 6 represents the main effects of the factors studied in these leaching experiments. Both the maximum recovery (%) of each experiment and the recovery after 120 min leaching time (which was often same than max.-% of recoveries) were chosen for the analysis. For both same trends can be observed. All leaching parameters studied in this work had significant effect on the dissolution of zinc. Only redox potential had negative response and all others leaching parameters (temperature, NaOH concentration, stirring rate and liquid-solid ratio) had positive response on zinc dissolution. However, the interactions of all factors were not easy to observe and to find out the interactions of these factors more experiments are needed.

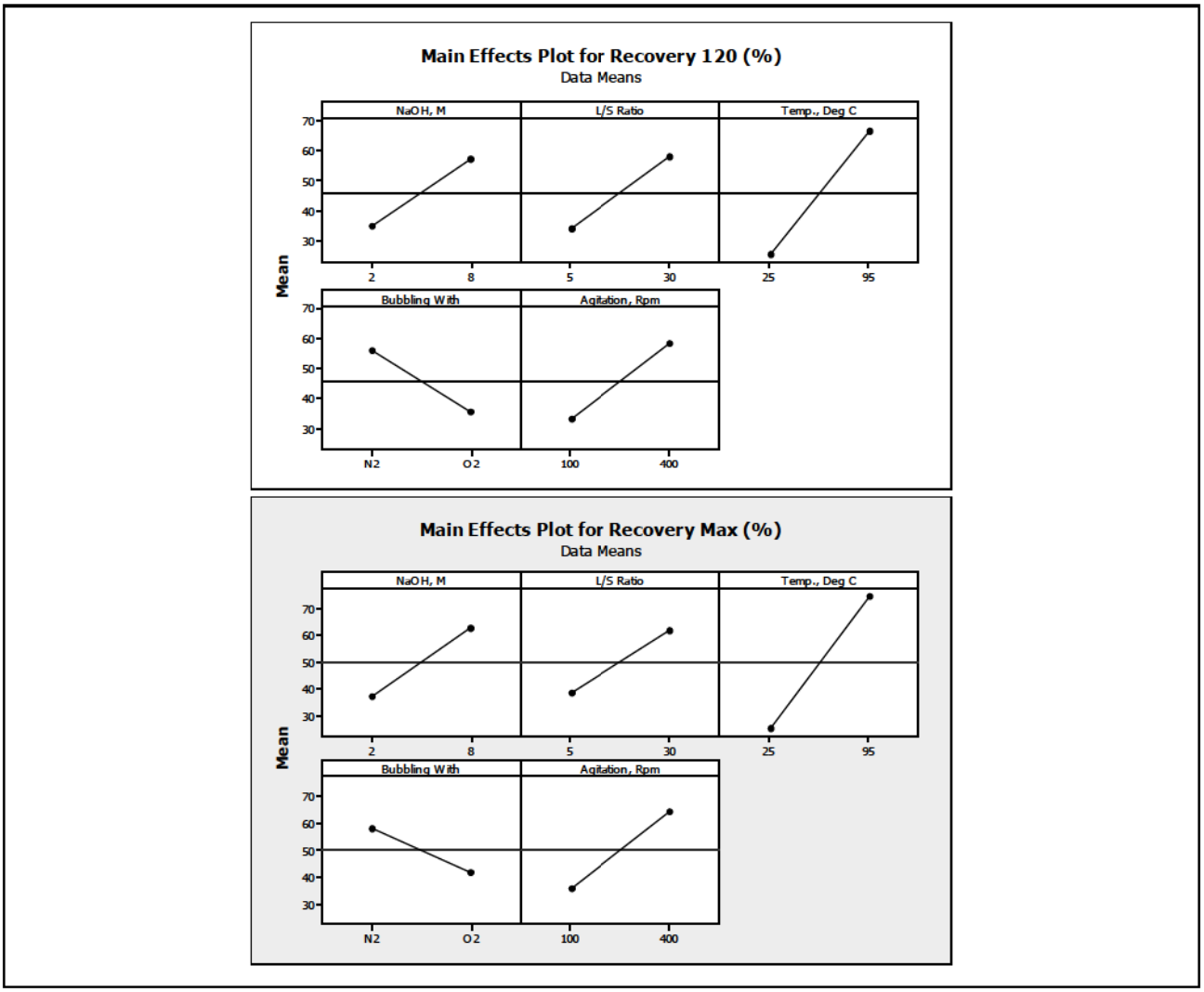

Figure 6: The main effects on leachability of zinc, a) after 120 min leaching, b) for max.-% recovery

Few samples after 120 min of leaching were analyzed more precisely in order to investigate that the unwanted iron and other elements were not leached. The results from these analyses are represented in Figure 7. These results support the leaching curves above that only zinc is leached in NaOH solution. Iron was not found to dissolve in these analyses and its amount was < 1.5 mg/l in the leach solution. Also the tests with ammonium thiocyanate (NH_4SCN) indicator showed that iron did not dissolve. In addition, the alloying elements are not leached substantially and the amounts in relation

to leached zinc are very low. Both analyses verify that zinc dissolves in NaOH solution while iron does not and the concentrations of alloying elements (Cr, Ni, Mo) are low in leachate solution.

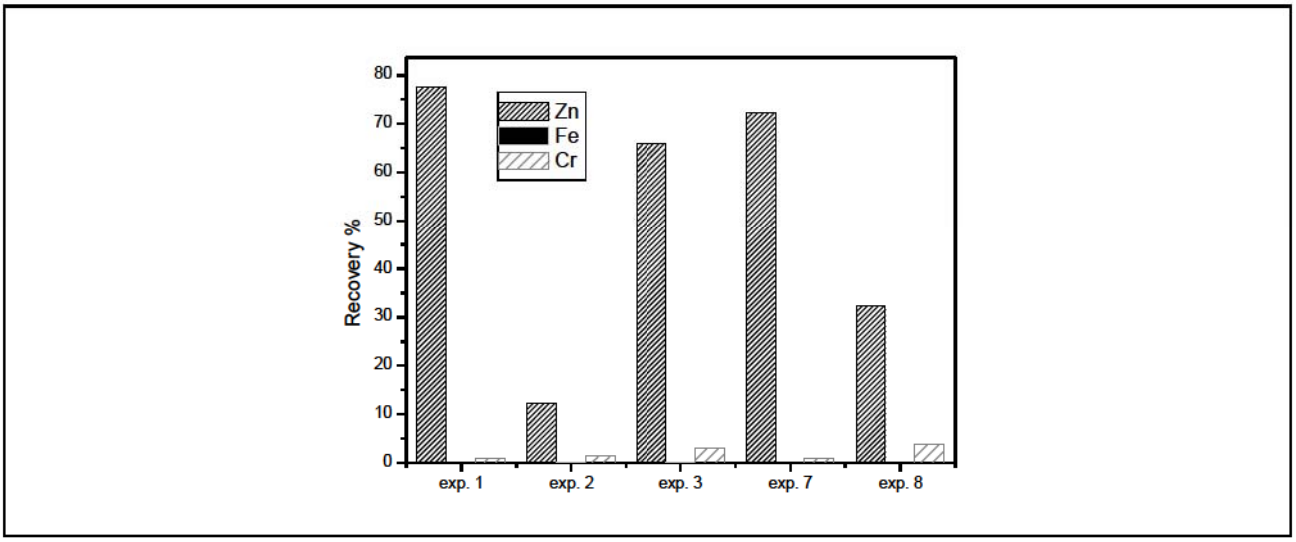

Figure 7: Recoveries (%) of Zn, Fe and Cr after 120 min leaching in few conditions. As iron is not leached (amount is < 1.5 mg/l) it does not show in the plot

6 Conclusions

The samples of AOD dust from stainless steel production, delivered from Outokumpu Stainless (Tornio, Finland), were leached in NaOH solution using different leaching conditions. The aim was to leach zinc out from the dust. The leaching experiments were done using factorial test series in which the effect of various leaching parameters was studied. The effect of NaOH concentration, temperature, solid-liquid ratio, stirring rate and redox potential were studied and all of them were found to affect the dissolution of zinc. The experiments showed that leaching with NaOH is selective and it is possible to leach zinc out from the dust. Iron was not leached from the dust and only minor amount of alloying elements was leached. Further experiments will be done in order to study the interactions of the leaching parameters.

Acknowledgement

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ALKALINE LEACHING OF STAINLESS STEEL PRODUCTION DUST

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Abstract
Stainless steel production generates quantities of dusts and sludge that are considered as harmful waste in most industrial countries. On the other hand, these dusts also contain valuable metals such as alloying elements. A direct recycling of dust back to steel production is hindered mainly due to the presence of zinc. Today dusts are recycled in separate treatment plants using predominantly pyrometallurgical processes. In this paper four different stainless steel dusts from Outokumpu Stainless (Tornio, Finland), were leached using NaOH solutions. The aim was to selectively leach zinc out from the dusts and minimize its amount in the dust residue. For all dusts, the best results for extracted zinc were achieved at 95 °C, with 8 M NaOH solution and stirring rate of 400 rpm. The maximum zinc extraction was 75 – 80 % from AOD1 dust, 55 – 60 % from EAF1 dust, 45 – 50 % from AOD2 dust and around 30 % from EAF2 dust. Difference in maximum zinc extraction arose from the mineralogical differences of the dusts. Zinc was leached selectively, of alloying elements only molybdenum was leached and practically no iron, chromium and nickel were dissolved.

Keywords: Stainless steels, dust, zinc, leaching, NaOH

1 Introduction

Stainless steel production generates quantities of various solid wastes in form of dusts and sludges. Between 30 and 70 kg of dust and fine waste is generated per ton of steel during the stainless steel production [1]. In most industrial countries stainless steel dusts are considered as harmful waste, on the other hand, these dusts also contain valuable metals such as alloying elements and zinc. Recovering them will save raw material costs and reduces environmental impact.

A direct recycling of dust back to stainless steel production is hindered because they contain considerable amounts of elements that cause operational difficulties in the steel making process [2]. Stainless steel dust consists mainly of oxide phases that are rich in Fe, Cr, Ca, Zn, Mg, Mn and Ni, with minor amounts of phases that contain alkaline metals (K, Na), halogens (Cl, F), Si, Mo, Pb and S [3]. The element that causes the most problems in treating flue dusts is zinc, which vaporizes easily and condenses into steel production fumes ending up in the flue dust or sludge usually as an oxide or ferrite. Zinc content in stainless steel dusts is usually in the range of 1.0 – 16.4 wt% [4-6].

Various pyrometallurgical, hydrometallurgical and combined processes have been developed to allow better utilization of steel making dusts in primary operations [2,7-11] but only few of them have reached commercialization. Today the dust treatment processes are predominantly pyrometallurgical and dusts are recycled in separate treatment plants. Metal extraction from the dusts is difficult due to their complex composition and finding a suitable treatment process is complicated as chemical compositions and crystalline phases present in the dusts vary

considerably. There are still significant problems treating these highly different materials and the developed processes have not been entirely satisfying [10]. The drawbacks with pyrometallurgical processes are the high consumption of energy and a need of relatively large tonnage of dust to be economically competitive.

The advantage with hydrometallurgical processes is that they are considered suitable for an on-site treatment [12] as they can fit on small scale [13]. Several hydrometallurgical methods for the recovery of zinc and other metals from these zinc-bearing wastes have been proposed but the major obstruction in the hydrometallurgical extraction of zinc has been the ferrite form of zinc. Zinc ferrite ($ZnFe_2O_4$) is insoluble [14] whereas ZnO dissolves easily in many solutions. The ratio of these phases of zinc depends on the type of furnaces and operations, especially the dust collection systems [12].

The choice between the processing routes depends strongly on the dust characteristic. Usually, the most important stage is the separation of the iron from non-ferrous metals such as zinc. Hydrometallurgical processes can offer an interesting alternative for zinc recycling if iron dissolution is controlled and zinc occurs mainly as ZnO in the dust. The major advantage of alkaline leaching is its selectiveness in leaching zinc compared to iron compounds. Thus a relatively clean and iron-free solution is obtained and the complicated iron removal processes are avoided.

In this paper we have studied selective alkaline leaching of zinc from stainless steel dusts and some process schemes. The target was to minimize the zinc content in the dust that would provide an opportunity to effectively recycle the dust back to the steel making process and to recover zinc from the dust.

2 Alkaline (NaOH) leaching

In hydrometallurgical processes, metals are extracted by a leaching stage and then recovered in metallic form by electrolysis or other reduction methods [15]. Principally, the two most used leaching methods for treating carbon steel dusts are sulfuric acid (H_2SO_4) and caustic soda (NaOH) leaching. The major advantage with acid solutions is that they are very familiar and cheap and with sulfuric acid solutions the traditional electrowinning is applicable to obtain metallic zinc [12]. However, in treating the steel making dusts a selective solubility of zinc relative to the iron compounds is critical in the leaching stage. The main problem with acids is that also iron dissolves and thus the solution purification process is difficult and complex. In addition, the high alkalinity of many dusts consumes a lot of acid for pH adjustment [2]. Alkaline leaching has the advantage that iron does not dissolve and a relatively clean iron-free leach solution can be achieved.

Alkaline leaching processes have been developed earlier and used for the leaching of zinc from the different oxidized ores and secondary materials. For example, Frenay et al. [16] developed the Cebedeau process (Fig. 1) for recovering metals from EAF dust. In the process, the dust was leached to dissolve zinc and lead in hot 95 °C concentrated 6 - 12 M NaOH solution for 1 - 2 hours. After leaching, lead was removed from the leachate using cementation with zinc powder. From the purified solution zinc was produced by electrolysis as powder. A commercial plant was built up in 1986 but was discontinued within a short time.

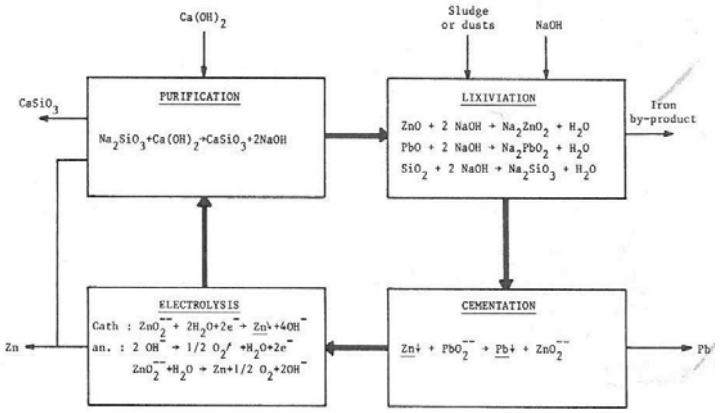

Fig. 1 Principle of the Cebedeau process [16]

The developed alkaline leaching processes have faced difficulties and have closed down. The Cebedeau process faced problems with the filtration for solid-liquid separation [7]. The solid-liquid separation is difficult with viscous NaOH solutions and extremely fine-grained solid, like dusts. However, it can be achieved with conventional equipment [7]. Other reason for failures is most likely that part of zinc in the dust is in ferrite form, when the total zinc recovery is limited by the amount of zinc present as zinc ferrite. Zinc ferrite is difficult to decompose, both in acidic and alkaline solutions [14]. Experiments have indicated that the maximum percentage of decomposed zinc ferrite has been only about 9% in NaOH leaching [10]. Despite that technical and economic problems have emerged, hydrometallurgical processes, such as caustic leaching, could offer some potential advantages for treating stainless steel dusts. A pyrometallurgical roasting step can be used to convert zinc ferrite into soluble zinc oxide to maximize zinc recovery [10].

The aim of the hydrometallurgical treating of dusts is to recover the valuable elements contained in the dust and to obtain a non-hazardous residue that can be stored without problems or can be used in agglomeration units in iron-making industries. The leaching process should produce a iron-bearing residue with maximum of 0.4 – 1 wt-% zinc in order to recycle it into the steel plant furnaces [7, 17]. To reach this objective a sequence of unit operations, such as leaching, filtration, purification, and precipitation or electrolysis processes is required. A simplified process flow sheet of the caustic soda leaching process for treating the dusts from stainless steel production is illustrated in Fig. 2.

Alkaline leaching, using sodium hydroxide as a leaching agent is seen effective in the dissolution of zinc, without significant dissolution of iron [13]. Also the solubility of Cr(III), Cu and Cd are found to be negligible. ZnO dissolves effectively with a strong NaOH solution and a leachate containing Zn as predominant element will be obtained. The leaching reaction (1) of zinc can be expressed as follows [7, 18]:

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O \qquad (1)$$

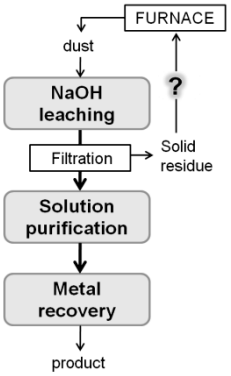

Fig. 2 A principal flowsheet of alkaline leaching process for treating the dust from stainless steel production.

After NaOH leaching the solids are separated from the leachate. A solid residue depleted in zinc and enriched in iron and chromium is obtained and it may be suitable for recycling back into furnaces in stainless steel production. After the solid-liquid separation a purification process is conducted to remove impurities, such as dissolved lead, from the leach liquor. For example, precipitation and cementation techniques can be carried out for that. Cementation is suitable for removing metals that are more noble than zinc from the solution, reaction (2) [7].

$$Me^{2+} + Zn^{0} \rightarrow Me^{0} + Zn^{2+} \quad (2)$$

Me = Cu, Pb, Cd, Ni, Co

However, the solubility of other metals in the dust is relatively low in NaOH solution, but lead dissolves quite easily. The residue from purification containing lead may be a suitable feed for a lead smelter [18]. After solution purification zinc can be recovered as solid zinc by electrolysis or precipitated as its pure compound. By hydrometallurgical processes can be produced a virgin quality of non-ferrous metals.

The cost/profitability of the process will be highly dependent on the zinc content of the waste and on the market value of the recovered zinc [19]. The same applies also to other metals. Important factors are also the cost of land filling and the sufficiency of raw materials from ores. The environmental legislation and the economics are the driving forces to treat the dust from stainless steel production. The environmental side is driven also by the economics of treatments but in the future dusts can be forced to be treated due to more stringent environmental legislation.

3 Materials and methods

Four different dust samples from stainless steel production were received from Outokumpu Tornio Works. AOD represents argon oxygen decarburization converter dust and EAF electric arc furnace dust. AOD1 and EAF1 dusts are generated from line 1 and AOD2 and EAF2 from line 2. Line 1 uses molten ferrochrome whereas in line 2 ferrochrome is melted with scrap in EAF. The dusts are a mixture of different production batches thus representing an average dust

composition. The chemical and mineralogical analysis of dust samples was done with optical microscopy, scanning electron microscopy (SEM), Electron probe micro-analyze (EPMA), X-ray diffraction (XRD), Atomic absorption spectroscopy (AAS), and Inductively coupled plasma atomic emission spectroscopy (ICP-AES) with molten sodium peroxide or nitric-hydrochloric acid leaching pre-treatment. The results from the chemical analyses are presented in Tab. 1. The main components in the dusts are iron, zinc, chromium and calcium. The zinc content was on average 9.8 % for AOD1, 7.3 % for EAF1, 5.2 % for AOD2 and 4.7 % for EAF2. Zinc was found to be present as zincite (ZnO) in AOD1 and as franklinite ($ZnFe_2O_4$) and zincite in AOD2, EAF1 and EAF2 dusts.

Tab. 1 The chemical composition of the dust samples

	Fe	**Cr**	**Zn**	**Ca**	**Mn**	**Mg**
AOD1	26.9 - 37.8	4.39 - 18.56	8.96 - 10.8	4.74 - 5.56	0.95 - 2.87	0 - 1.38
AOD2	13.8 - 26.4	2.18 - 13.39	3.52 - 5.91	13.08 - 17.2	0.9 - 3.4	0 -2.53
EAF1	14.4 - 23.0	1.69 - 18.16	5.44 - 8.27	8.64 - 11.36	1.24 - 3.56	0 - 2.77
EAF2	10 - 20	1.59 - 17.19	3.56 - 6.4	10.94 - 15.1	0.98 - 3.06	0 - 1.41
	Ni	**Pb**	**Si**	**Mo**	**K**	
AOD1	0.4 - 0.72	0.08 - 0.1	0 - 0.89	0 - 0.075	0 - 0.93	
AOD2	1.88 - 2.92	0.39 - 0.56	0 - 2.76	0 - 1.4	0 - 0.85	
EAF1	0.84 - 1.49	0.39 - 0.65	0 - 4.25	0 - 1.38	0 - 1.38	
EAF2	1.38 - 2.61	0.86 - 1.11	0 - 4.11	0 - 0.15	0 - 1.4	
Minor amounts 0 - < 1 %	**Al, B, Ba, C, Cd, Co, Cu, F, Na, P, S, Sr, V**					

The experimental setup for the leaching test consisted of a termobath (Lauda AquaLine AL25), glass reactor and motor driver stirrer (VWR VOS16). The lid of glass reactor provided holes for mercury thermometer, gas bubbling, stirrer and sampling/feeding. A water-cooled condenser was used higher temperatures. In all tests 800 ml NaOH solution from technical grade grains and distilled water at concentrations of 2M or 8M was used. Temperature of the reactor was controlled with a water bath to 25 °C or 95 °C. For adjusting the oxidative or reductive conditions, oxygen or nitrogen gas was fed into the reactor for 1 hour and after that 160 g or 26.67 g of dust (=liquid/solid ratios of 5 or 30) was charged and stirring rate of 100 rpm or 400 rpm was adjusted.

A liquid sample was taken off and filtered in the chosen time intervals of 5, 15, 30, 60 and 120 minutes. The stirring was stopped 30 seconds before each sampling. After filtering the leach samples were analysed for the amount of leached Zn with Perkin Elmer 372 AAS device. Part of the samples after 120 min of leaching was analyzed more precisely with multi-element ICP-AES analysis.

4 Results and discussion

The main response under investigation was the percentage of zinc extraction from the dusts in the leach liquor. From the experimental test series, two leaching conditions gave higher zinc extractions than the other. The leaching curves of zinc at these conditions are presented in Fig. 3. The extractions were greater with AOD1 and EAF1 dusts from line 1 and were 75 - 80 % for AOD1 dust and 55 - 60 % for EAF1 dust. The highest zinc extractions for the dusts from line 2 were 45 – 50 % for AOD2 dust and around 30 % for EAF2 dust. Difference in the maximum

zinc extractions arose most likely from the mineralogical differences of the dusts and is dependent on the amount of zinc in ferrite from. Zinc ferrite phase was identified in AOD2, EAF1 and EAF2 dusts. For the maximum extractions of zinc strong 8M NaOH solution and high temperature of 95 °C was needed. Also strong agitation was desirable. The dissolution of zinc was fast and the most of the leachable zinc is dissolved in few minutes.

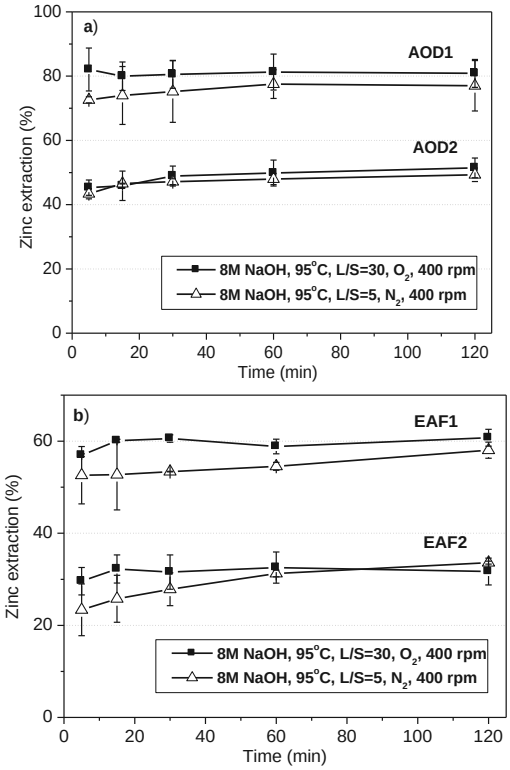

Fig. 3 Leaching curves of zinc for both a) AOD and b) EAF dusts.

Some of the samples after 120 min of leaching were analyzed with ICP-AES in order to investigate that iron and other elements such as alloying elements were not leached. The results showed that practically no iron (< 1.5 mg/l) or nickel (< 0.1 mg/l) was dissolved. The extractions of zinc, chromium and molybdenum in 8 M NaOH solution at temperature of 95 °C and stirring rate of 400 rpm with L/S ratio of 30 and oxygen bubbling are presented in Fig. 4. Chromium was dissolved around 4 % at most whereas 68 – 100 % of molybdenum was dissolved. Solubility of molybdenum in strong NaOH solutions clearly differed from the other alloying elements. In AOD2 dust phases containing molybdenum were identified and the amount (mg/l) of molybdenum was almost the same than zinc in the leachates from AOD2 dust, in couple samples it was even slightly higher. In other dusts the amount of Mo was low compared to AOD2 dust and thus also its amount (mg/l) was low in relation zinc in the leachates.

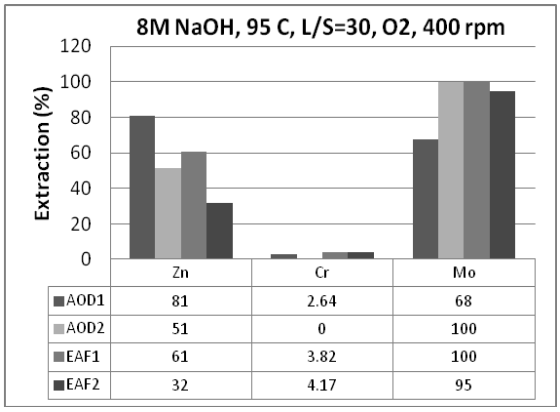

Fig. 4 The extraction of zinc, chromium and molybdenum in strong and hot NaOH solution

5 Conclusions

Four different dust samples from stainless production, delivered from Outokumpu Stainless (Tornio, Finland), were leached in NaOH solution using different leaching conditions. The aim was to selectively leach zinc out from the dust and minimize its amount in dust residue. The dust samples were leached under atmospheric pressure and the studied leaching variables were temperature, sodium hydroxide concentration, liquid to solid ratio (L/S), stirring rate and oxygen or nitrogen gas bubbling. For all dusts, the highest amounts of extracted zinc were achieved at 95 °C, with 8M NaOH solution and stirring rate of 400 rpm. The maximum zinc extraction was 75 – 80 % from AOD1 dust, 55 – 60 % from EAF1 dust, 45 – 50 % from AOD2 dust and around 30 % from EAF2 dust. The extractions were greater for the dust from line 1. Difference in maximum zinc extraction arose from the mineralogical differences of the dusts. Zinc ferrite phase was identified in AOD2, EAF1 and EAF2 dusts. The experiments showed that leaching of zinc using NaOH solutions is selective.Of the alloying elements only molybdenum was leached and practically no iron, chromium and nickel dissolved. Further experiments will be needed in order to study the solid-liquid separation, purification of the leachate and zinc recovery from the leachate.

Acknowledgements

This work has been done in the METDUST project of the ELEMET research program funded by FIMECC Oy. The financial support of TEKES, Outokumpu Stainless Oyj and Outotec Oyj is gratefully acknowledged. The analytical work in characterizing the dusts done by the group of Professor Tomas Havlik in Technical University of Kosice and M.Sc. Hannu Makkonen from Oulu University is gratefully acknowledged.

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ALKALINE LEACHING OF ZINC FROM ARGON OXYGEN DECARBONIZATION DUST FROM STAINLESS STEEL PRODUCTION

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Abstract: Stainless steel production generates solid wastes such as dust and sludge that are considered as harmful in most industrial countries. Today dusts are recycled in separate treatment plants as these dusts contain valuable metals such as alloying elements. A direct recycling of dust back to steel production is hindered due to the presence of elements, especially zinc, that cause operational difficulties in the stainless steel making process. In this paper two different stainless steel converter argon oxygen decarbonization dusts (AOD1 and AOD2), from Outokumpu Stainless (Tornio, Finland), were leached using NaOH solutions. The purpose was to selectively leach zinc out from the dusts and to find factors that affected most dissolution of zinc. The dust samples were leached under atmospheric pressure and the factors tested were temperature, sodium hydroxide concentration, liquid to solid ratio (L/S), stirring rate and oxygen or nitrogen gas bubbling. All the studied factors had statistically significant effect on the dissolution of zinc. The maximum zinc extraction was achieved at 95°C, with 8M NaOH solution, stirring rate of 400 rpm and L/S ratio of 30 and was around 80% for AOD1 dust and around 50% for AOD2 dust. Difference in maximum zinc extraction arose from the mineralogical differences of the dusts. Zinc was leached selectively. Among alloying elements only molybdenum was leached and practically no iron, chromium and nickel were dissolved.

Key words: *AOD dust, stainless steel, zinc, leaching, sodium hydroxide*

Introduction

Stainless steel production generates quantities of various solid wastes in form of dust and sludge. During the production of stainless steel, between 30 and 70 kg of dust and fine waste is generated per ton (megagram) of steel produced (Denton, 2005). In most industrial countries stainless steel dusts are considered as harmful waste, on the other hand, these dusts also contain valuable metals such as alloying elements and zinc. From economic and environmental point of view it is desirable to recover the valuables and utilize these wastes (Majuste, 2009). However, a direct recycling of dust back

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to stainless steel production is hindered because they contain considerable amounts of elements, especially zinc, that cause operational difficulties in the steel making process (Palencia, 1999). Zinc vaporizes easily and condenses into steel production fumes ending up in the flue dust or sludge usually as an oxide or ferrite and its content in stainless steel dusts is in the range of 1.0–16.4 wt% (Atkinson, 2001; Leclerc, 2002; Nyirenda, 1992).

Various pyrometallurgical, hydrometallurgical and combined processes have been developed to allow better utilization of steel making dusts in primary operations (Jha, 2000; Orhan, 2005; Rao, 2006; Xia, 1999; Youcai, 2000) but only few of them have reached commercialization. Today the dust treatment processes are predominantly pyrometallurgical and dusts are recycled in separate treatment plants to recover metals. There are still significant problems associated with treating this material and the developed processes have not been entirely satisfying (Xia, 1999). The drawbacks with pyrometallurgical processes are the high consumption of energy and a need of relatively large tonnage of dust to be economically competitive. Hydrometallurgical processes are considered suitable for an on-site treatment (Nakamura, 2007) as they can fit on small scale (Dutra, 2006), but the major obstruction in the hydrometallurgical extraction of zinc is the ferrite form of zinc. Zinc ferrite ($ZnFe_2O_4$) is insoluble in many solutions (Xia, 2000) and usually 30–70% of zinc is in ferrite form (Leclerc, 2002).

Metal extraction from the dusts is difficult due to their complex composition. Stainless steel dust consists mainly of oxide phases that are rich in Fe, Cr, Ca, Zn, Mg, Mn and Ni, with minor amounts of phases that contain alkaline metals (K, Na), halogens (Cl, F), Si, Mo, Pb and S (Ma, 2006). However, the chemical compositions and crystalline phases present in the dusts vary considerably depending on the steel grade produced, raw materials used, and operation conditions and procedures (Rao, 2006). Finding a suitable process is complicated as each dust is unique. Hydrometallurgical processes can offer an interesting alternative for zinc recycling if iron dissolution can be controlled. The major advantage of alkaline leaching is its selectiveness in leaching zinc compared to iron compounds. Thus, a relatively clean and iron-free solution is obtained and the complicated iron removal processes are avoided.

Previous studies on hydrometallurgical methods have concentrated on the leaching of zinc from carbon steel dusts and mainly from the electric arc furnace (EAF) dusts. In this paper two different argon oxygen decarbonization converter dusts (AOD1 and AOD2) from stainless steel production (Outokumpu Stainless Oy Tornio, Finland) were leached using NaOH solutions. The target was to selectively leach zinc out of stainless steel making dusts and to minimize the zinc content in the dust. This would provide an opportunity to effectively recycle the dust back to the steel making process and to recover zinc from the dust.

Experimental

Argon oxygen decarburization converter dust samples (AOD1 and AOD2) from stainless steel production were received from Outokumpu Tornio Works for the leaching experiments. AOD1 represents dust from line 1 and AOD2 from line 2. On line 1 ferrochrome is fed as melt into AOD converter whereas on line 2 solid ferrochrome is melted along with the charge. The dusts are a mixture of different production batches thus representing an average dust composition.

The chemical and mineralogical analysis of dust samples was done with optical microscopy, Scanning electron microscopy (SEM), Electron probe micro-analyzer (EPMA), X-ray diffraction (XRD), Atomic absorption spectroscopy (AAS), and Inductively coupled plasma atomic emission spectroscopy (ICP-AES) with molten sodium peroxide or nitro-hydrochloride acid leaching pre-treatment. The results of the chemical analyses are presented in Table 1. The main components in the dusts are iron, zinc, chromium and calcium. The zinc content is on average 9.762% for AOD1 and 4.650% for AOD2. The identified phases in the AOD1 and AOD2 dusts, according to qualitative phase analysis, are presented in Table 2. Zinc was found to be present as zincite (ZnO) in AOD1 as franklinite ($ZnFe_2O_4$) and zincite in AOD2. In the AOD2 dust, there were phases that contained a significant amount of molybdenum.

Table 1. The chemical composition of dust samples (in %)

	Fe	Cr	Zn	Ca	Mn	Mg	Ni	Pb	Si	Mo
AOD1	26.9–37.8	4.39–18.56	8.96–10.8	4.74–5.56	0.95–2.87	0–1.38	0.4–0.72	0.08–0.1	0–0.89	0–0.075
AOD2	13.8–26.4	2.18–13.39	3.52–5.91	13.08–17.2	0.9–3.4	0–2.53	1.88–2.92	0.39–0.56	0–2.76	0–1.4
Minor amounts 0–< 1% in both dusts	Al, B, Ba, C, Cd, Co, Cu, F, K, Na, P, S, Sr, V									

Table 2. The identified phases according to qualitative phase analysis

Element	AOD1	AOD2
Fe, Cr, Mg	$FeCr_2O_4$ (chromite), $MgFe_2O_4$ (magnesioferrite), Fe_3O_4 (magnetite), $(NiFe)Fe_2O_4$ (trevorite), $MgFe_2O_4$ (magnesioferrite), Fe_2O_3 (maghemite)	$MgFe_2O_4$ (magnesioferrite), Fe_3O_4 (magnetite), $FeCr_2O_4$ (chromite), $ZnFe_2O_4$ (franklinite), $(NiFe)Fe_2O_4$ (trevorite), Fe_2O_3 (maghemite), $(FeMg)(CrFe)_2O_4$ (donathite)
Zn	ZnO (zincite)	$ZnFe_2O_4$ (franklinite), ZnO (zincite)
Ni	NiO (bunsenite), $(NiFe)Fe_2O_4$ (trevorite)	$(NiFe)Fe_2O_4$ (trevorite)
Ca	CaO (lime)	CaO (lime), $CaCO_3$ (calcite)
Si	$(NH_4)_2SiF_6$ (cryptohalite)	$(NH_4)_2SiF_6$ (cryptohalite)
Mn		KMn_8O_{16} (cryptomelane)
Mo		MoO_2 (tugarinovite)

The microstructure of the dusts consists of bigger particles and grains surrounded by finer fraction. Also agglomeration of finer fraction was noticed. The particle size analysis of dust samples was done with laser diffraction (Beckman Coulter) and by Scanning-Foto-Sedimentograf. All particles measured by Scanning-Foto-Sedimentograf were under 47 μm for both AOD1 and AOD2 dusts with smallest particles under 1 μm. Analyses by laser diffraction showed that all particles were less than 4 μm for AOD1 dust and 20 μm for AOD2 dust. Larger particles consist of several phases and some phases were encapsulated inside of particles. For the finer fraction no encapsulation phenomenon was found. Zinc occurred mainly in the fine fraction in which the maximum ZnO content is around 14% in both AOD1 and AOD2 dusts.

The leaching experiments were carried out in the apparatus shown in Figure 1. The experimental setup for the leaching test consisted of a termobath (Lauda AquaLine AL25), glass reactor and motor driver stirrer (VWR VOS16). The cover of the glass reactor provided through holes for mercury thermometer, gas bubbling, stirrer and sampling/feeding. A water-cooled condenser was added to the structure at higher temperatures.

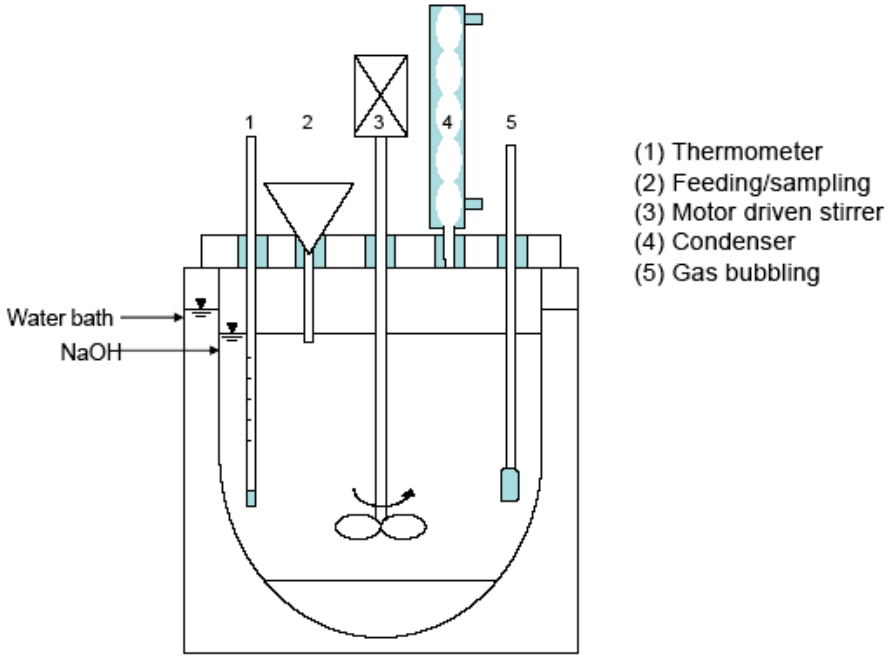

Fig. 1. Leaching reactor in water bath

Volume of 800 cm^3 of NaOH solution (prepared by technical grade grains and distilled water) was set into the reactor, which was put in a water bath in order to control the temperature in the reactor. For adjusting the oxidative or reductive conditions,

oxygen or nitrogen gas was fed into the reactor for 1 hour and after that the dust was charged and stirring rate was adjusted. A liquid sample was taken off and filtered in the chosen time intervals of 5, 10, 15, 20, 25, 30, 60 and 120 minutes for AOD1 dust and 5, 15, 30, 60 and 120 minutes for AOD2 dust. The stirring was stopped 30 seconds before each sampling.

The leaching tests were done using factorial test series (Table 3) with two replicates where a high and a low level of a factor were used. The studied factors were temperature, NaOH concentration, liquid-solid ratio (cm^3/g), stirring rate and oxygen or nitrogen gas bubbling. In the experiments temperature of 25°C or 95°C and NaOH concentrations of 2 M and 8 M were used. The chosen liquid/solid (cm^3/g) ratios were 5 and 30 and for this 160 g or 26.67 g of dust was added to the reactor. The stirring rate was adjusted to 100 or 400 rpm and the oxidative or reductive conditions were adjusted using oxygen or nitrogen gas bubbling.

Table 3. Factorial (2^{5-2}) test series used in the leaching experiments

Std Order	NaOH (M)	L/S Ratio	Temp. Deg C	Bubbling with	Agitation rpm
1	2	5	25	O_2	400
2	8	5	25	N_2	100
3	2	30	25	N_2	400
4	8	30	25	O_2	100
5	2	5	95	O_2	100
6	8	5	95	N_2	400
7	2	30	95	N_2	100
8	8	30	95	O_2	400

After filtering the leach samples were analysed for the amount of leached Zn, with the Perkin Elmer 372 AAS device. The standard solutions were prepared by using an Atomic Absorption Standard zinc 1000 $\mu g/cm^3$ Baker 6827 solution. Part of the samples after 120 min of leaching was analyzed more precisely with multi-element ICP-AES analysis in order to investigate that the unwanted iron and other elements were not leached.

Results and discussion

The main response under investigation was the percentage of zinc extraction from the AOD1 and AOD2 dusts in the leach liquor. The leaching curves of zinc are presented in Figs 2 and 3. Figure 2 shows the leaching curves of the four experimental conditions with best zinc recovery. In Fig. 3 the four leaching conditions of lower zinc extractions are shown. From the shape of the leaching curves can be observed that the dissolution of zinc is fast (in the both high and low recoveries of zinc) and occurs in a

few minutes. Usually, the maximum recovery was achieved at the longest leaching time (120 min), however, in some experiments the maximum yield of zinc was achieved earlier and then it decreased, which may indicate that part of zinc was precipitated back.

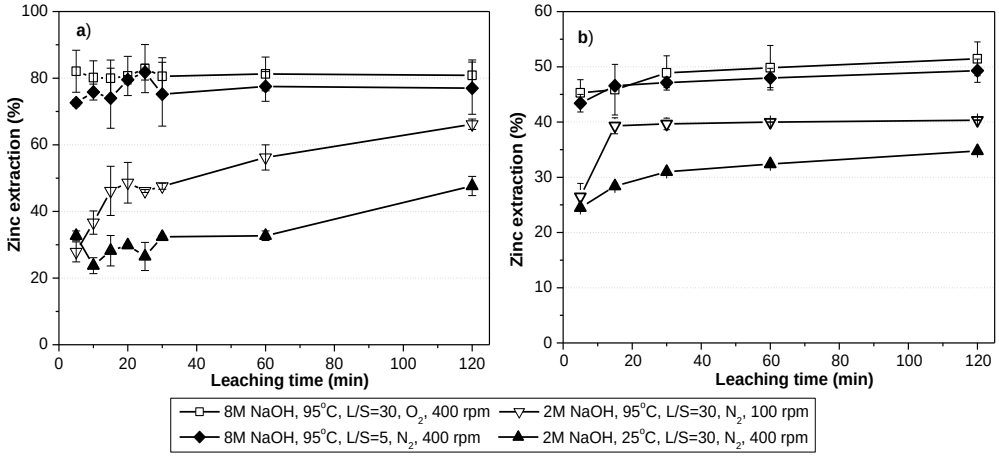

Fig. 2. The four leaching conditions that gave better zinc extractions for a) AOD1 and b) AOD2 dust

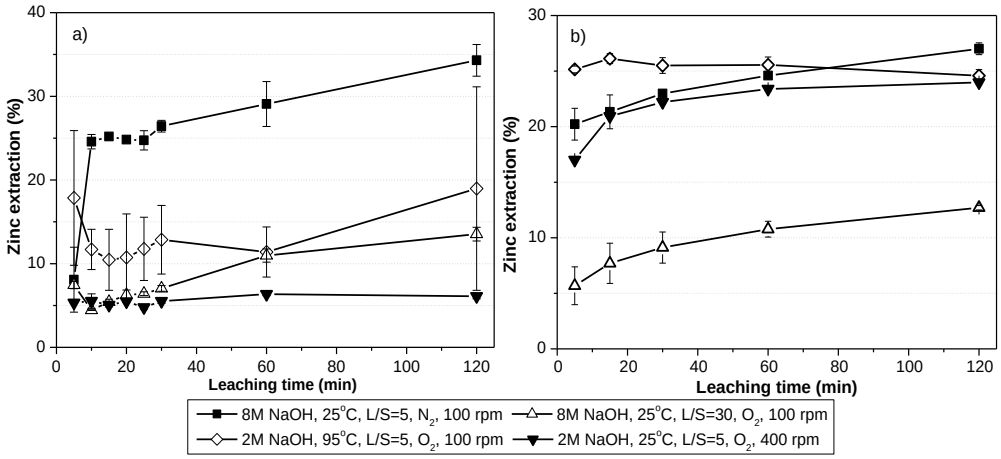

Fig. 3**.** The four leaching conditions that gave poorer zinc extractions for a) AOD1 and b) AOD2 dust

Under the present experimental conditions, zinc extraction varied from 6% to around 80% for the AOD1 dust. The extractions were on the average lower for AOD2 dust and varied from 13% to around 50%. Difference in maximum zinc extraction arose from the mineralogical differences of the dusts. In the AOD2 dust zinc was found to be present also in ferrite form that is difficult to dissolve in alkaline solutions.

For both dusts the maximum value of extracted zinc was obtained by using 8 M NaOH solution and stirring rate of 400 rpm at the temperature of 95°C. The liquid-solid ratio was 30 and oxygen bubbling was used. According to the results the dissolution of zinc was greater when high temperature and stirring rate, strong NaOH solution and lower liquid-solid ratio were used.

To study the effects and possible interactions of the leaching factors on zinc dissolution, the analysis was done using the Minitab 16 software. Figure 4 represents the normal plot of the standardized effects of the studied factors after 120 min leaching.

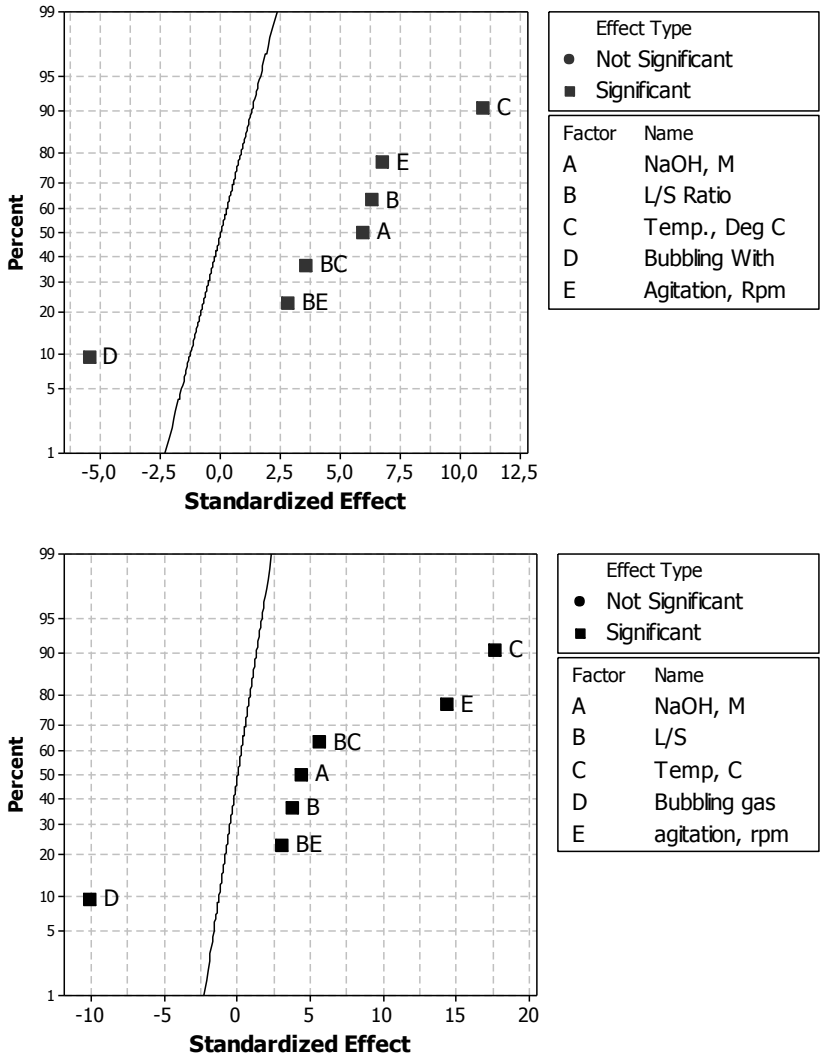

Fig. 4. Normal plot of the standardized effects of studied factors (response is Zn extraction %, alpha = 0.05). Above: AOD1 dust. Below: AOD2 dust

Mainly, the same trends can be observed for both dusts. All leaching factors studied in this work had statistically significant effect on the dissolution of zinc. Temperature affected the zinc extraction preferentially in both dusts and the other factors were nearly equally significant for the AOD1 dust. For AOD2 dust, temperature, agitation and bubbling gas were more significant factors when NaOH concentration and L/S ratio were less significant. For both dusts, temperature, NaOH concentration, stirring rate and liquid-solid ratio had a positive response on zinc dissolution and increasing values of these factors increased the dissolution of zinc. Oxygen bubbling had a negative response and the dissolution of zinc was enhanced with nitrogen gas bubbling although the highest zinc extraction was achieved under conditions in which oxygen bubbling was used.

The interactions of all factors were not easy to observe, nevertheless, two-factor interactions were found between NaOH concentration and other studied factors in both dusts (Fig. 5). The interactions with NaOH concentration, stirring rate and temperature are explained by the high viscosity of strong NaOH solution. The increase of temperature and/or stirring rate enhanced the extraction of zinc in strong viscous NaOH solution. Also a strong 8 M NaOH solution is needed for leaching zinc when the amount of solids was larger. The reason for interaction between NaOH concentration and bubbling gas is unclear. It is possible that there is not significant electrochemical dissolution, where the oxidant could have an effect. To find out the possible interactions between the other factors more experiments are needed.

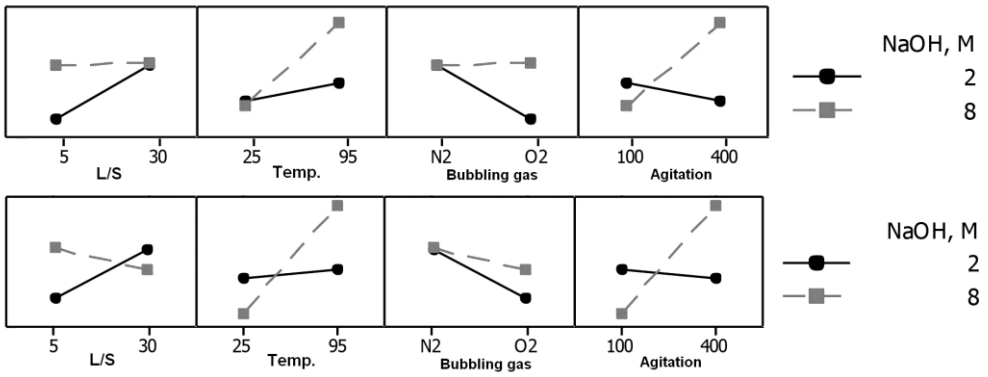

Fig. 5. Two-factor interactions between NaOH concentration and other studied factors after 120 min of leaching. Above: AOD1 dust. Below: AOD2 dust

Some of the samples after 120 min of leaching were analyzed with ICP-AES in order to investigate that iron and other elements such as alloying elements were not leached. The results for iron, chromium, nickel and molybdenum are presented in Table 4. Practically no iron (< 1.5 mg/dm^3) or nickel (< 0.1 mg/dm^3) was dissolved. Chromium was dissolved less than 4% at most. Solubility of molybdenum in strong NaOH solutions differed from the other alloying elements. Molybdenum dissolved

well and its amount (mg/dm^3) was almost the same as zinc in the leachates from the AOD2 dust. In couple of samples it was even slightly higher. In the AOD1 dust the amount of Mo was low compared to the AOD2 dust and thus also its amount (mg/dm^3) was low in relation to zinc in the leachate from the AOD1 dust.

Table 4. Amount of certain elements in leachate after 120 min leaching

	Amount in leachate (mg/dm^3)							
	Zn	Fe	Cr	Ni	Mo	Ca	Pb	Cd
AOD1	394–14950	< 1.5	27–484	< 0.1	3–56	< 5–21	< 2.5–24	< 0.25
AOD2	194–3722	< 1.5	< 1–258	< 0.1- 0.11	193–2834	< 5–10	< 2.5–61	< 0.25

Conclusions

Two different AOD dust samples from stainless production, delivered from Outokumpu Stainless (Tornio, Finland), were leached in NaOH solution using different leaching conditions. The purpose was to selectively leach zinc out from the dusts and to find factors that affected most on dissolution of zinc. The leaching experiments were done using factorial (2^{5-2}) test series and the studied factors were NaOH concentration, temperature, solid-to-liquid ratio, stirring rate and oxygen or nitrogen gas bubbling. All factors had statistically significant effect on the dissolution of zinc in both dusts and the effect of temperature was emphasized. All factors had positive response except oxygen gas bubbling, that had negative response. In both dusts the maximum zinc extraction was achieved at 95°C, with 8M NaOH solution, stirring rate of 400 rpm and L/S ratio of 30. Maximum zinc extraction was 80% from the AOD1 dust and 50% from the AOD2 dust. Difference in maximum zinc extraction arose from the mineralogical differences of the dusts. In the AOD2 dust zinc was found to be present also in ferrite. The experiments showed that leaching of zinc using NaOH solutions is selective, among alloying elements only molybdenum was leached and practically no iron, chromium and nickel were dissolved.

Acknowledgement

This work has been done in the METDUST project of the ELEMET research program funded by FIMECC Oy. The financial support of TEKES, Outokumpu Stainless Oyj and Outotec Oyj is gratefully acknowledged. The analytical work in characterizing the dusts done by the group of Professor Tomas Havlik in Technical University of Kosice and M.Sc. Hannu Makkonen from Oulu University is gratefully acknowledged. The authors are grateful to Mr. Terry Russell for the valuable guidance in data analysis.

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ALKALINE LEACHING OF ZINC FROM STAINLESS STEEL ELECTRIC ARC FURNACE DUSTS

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Abstract: Stainless steel production generates dust and sludge that are considered as a harmful waste. These dusts contain also valuable metals but extraction and recovery of valuables is difficult due their complex composition. Zinc is the most troublesome element in the dust and it hinders direct recycling of dust back into furnaces. In this paper two different stainless steel electric arc furnace dusts (EAF1 and EAF2) from Outokumpu Stainless (Tornio, Finland), were leached using NaOH solutions. The purpose was to selectively leach out zinc from the dusts and to find factors that affected most dissolution of zinc. From all leaching factors temperature, agitation speed and NaOH concentration were found to be statistically strongly significant, whereas a liquid-to-solid ratio and bubbling gas were only somehow significant. Two experiments from the test series gave clearly higher zinc extraction, that is around 60% for EAF1 and 30% for EAF2. For those experiments, a strong 8 M NaOH solution with the high temperature and agitation speed was used but bubbling gas and liquid-to-solid ratio changed. Zinc was leached selectively and practically no iron, chromium and nickel dissolved.

Keywords: *electric arc furnace dust, EAF, stainless steel, zinc, leaching, sodium hydroxide*

Introduction

Stainless steel production generates large quantities of various solid wastes in form of dust and sludge. During production of stainless steel, between 30 and 70 kg of dust and fine waste is generated per mega gram of steel produced (Denton, 2005). Their disposal or possible re-use has been a serious concern for an industry as in most industrial countries stainless steel dusts are considered as a harmful waste. On the other hand, the stainless steel dusts contain valuable metals such as alloying elements like chromium, nickel and molybdenum, and zinc from recycling of galvanized scrap. From economic and environmental point of view, it is desirable to recover the valuables and utilize these wastes (Majuste, 2009). Direct recycling of dust back to stainless steel production is however hindered, mainly because of zinc content of the

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dust. Zinc vaporizes easily and condenses into steel production fumes ending up in the flue dust or sludge usually as oxide or ferrite. Zinc content in the stainless steel dusts is found to vary from 1.0 to 16.4 wt% (Nyirenda, 1992; Atkinson, 2001; Leclerc, 2002; Laforest, 2006).

A number of pyrometallurgical, hydrometallurgical and combined processes have been developed to allow better utilization of steel making dusts in primary operations (Xia, 1999; Youcai, 2000; Jha, 2000; Orhan, 2005; Havlik, 2006; Rao, 2006b) but only few of them have reached commercialization. Today, the dust treatment processes are predominantly pyrometallurgical and dusts are recycled in separate treatment plants. However, the drawbacks with pyrometallurgical processes are: high energy consumption, production of a raw zinc oxide with low commercial value, and need of relatively large tonnage of dust to be economically competitive (Nakamura, 2005; Oustadakis, 2010; Rao, 2006b). Hydrometallurgical processes are considered to be suitable for on-site treatment as they can fit on small scale and thus offer interesting alternative (Nakamura, 2008).

Principally, two most studied leaching methods for treating carbon steel dusts are sulfuric acid (H_2SO_4) and caustic soda (NaOH) leaching. The benefit with acid solutions is that they are very accessible and cheap, but the drawbacks are that also iron contained in the dust dissolves and high alkalinity of many dusts consumes a lot of acid for pH adjustment (Palencia, 1999). The major advantage of alkaline leaching is selective solubility of zinc compared to iron compounds, and thus a relatively clean and iron-free solution is obtained, and the complicated iron removal process is avoided. So far, the major obstruction in hydrometallurgical extraction of zinc has been the presence of zinc ferrite ($ZnFe_2O_4$) in the dust, which is insoluble in many solutions (Havlik, 2006). Usually 30–70% of zinc is in a ferrite form (Leclerc, 2002), but to enhance the zinc recovery, a low temperature roasting step prior to alkaline leaching can be used to convert zinc ferrite into soluble zinc oxide (Xia, 1999).

Dusts from stainless steel production contain many elements making metal extraction very complex and difficult. The stainless steel dust consists mainly of oxide phases that are rich in Fe, Cr, Ca, Zn, Mg, Mn and Ni, with minor amounts of phases that contain alkaline metals (K, Na), halogens (Cl, F), Si, Mo, Pb and S (Ma, 2006). However, chemical compositions and crystalline phases present in the dusts vary considerably depending on the steel grade produced, raw materials used, and operation conditions and procedures (Rao, 2006a). The composition of stainless steel dusts differs substantially from unalloyed steel dusts and typically the stainless steel flue dusts are richer in alloying elements such as chromium, nickel and manganese, but lower in zinc and lead. The previous studies on the hydrometallurgical methods have concentrated on leaching of carbon steel dusts, and for this purpose both acid and alkaline leaching-based laboratory and pilot set-ups have been constructed. Only few studies of acidic leaching of dusts from stainless steel production are found (Majuste, 2009; Kekki, 2012).

In this paper two different stainless steel electric arc furnace dusts (EAF1 and EAF2) from Outokumpu Stainless (Tornio, Finland) were leached using NaOH solutions. The purpose was to selectively leach out zinc from the dusts and to find factors that affected most on dissolution of zinc. Also possible interactions of the studied leaching factors were observed. Alkaline leaching was chosen because of its selectiveness in leaching of zinc when compared to iron compounds.

Materials and methods

Electric arc furnace dust samples (EAF1 and EAF2) from stainless steel production were received from Outokumpu Tornio Works for the leaching experiments. The EAF1 represents dust from line 1 and the EAF2 from line 2. Line 1 uses molten ferrochrome, whereas in line 2 ferrochrome is melted with scrap in EAF. The dusts are a mixture of different production batches, thus represent an average dust composition.

The chemical and mineralogical analyses of dust samples were executed with thw optical microscopy, scanning electron microscopy (SEM), electron probe micro-analyzer (EPMA), X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) with molten sodium peroxide or nitro-hydrochloride acid leaching pre-treatment. The dust samples were also subjected in a particle size analysis by a scanning-foto-sedimentograf. The results from the chemical and mineralogical analyses are given in Tables 1 and 2. The

Table 1. The chemical composition of the dust samples

	Fe	Cr	Zn	Ca	Mn	Ni	Pb	Mg[a]	K[a]	Si[b]
EAF1	19.75 ±1.64	8.07 ±3.03	7.27 ±0.54	10.35 ±0.46	2.47 ±0.45	1.28 ±0.14	0.54 ±0.05	2.59 ±0.15	1.32 ±0.04	4.25
EAF2	16.39 ±1.84	8.10 ±2.95	5.20 ±0.58	13.48 ±0.72	2.14 ±0.40	2.14 ±0.23	0.97 ±0.05	1.24 ±0.17	1.35 ±0.01	4.11
Minor amounts 0 - < 1 % in both dusts	Al, B, Ba, C, Cd, Co, Cu, F, Mo, Na, P, S, Sr, V									

[a] calculation is based on three analyses, [b] found only in one analysis

Table 2. The main phases identified in dust samples from XRD analysis (Kukurugya, 2013)

EAF1	EAF2
$FeCr_2O_4$	$FeCr_2O_4$
$ZnFe_2O_4$	$ZnFe_2O_4$
$Ni_{0.25}Fe_{0.75}Fe_2O_4$	$NiFe_2O_4$
ZnO	CaO
CaO	$CaCO_3$
	MnO_2

main components in the dusts are iron, zinc, chromium and calcium. Zinc was found to be present as zincite (ZnO) and as franklinite ($ZnFe_2O_4$) in both dusts. The microstructure of dusts consists of larger particles and grains surrounded by finer fraction. The particle size for both dusts was around 1–50 μm. Larger particles often consist of several phases and some phases were encapsulated inside of particles. A part of zinc was found in a concentrate into a fine fraction.

The leaching tests were performed using a 2^{5-2} fractional factorial design with two replicates, where the high and low levels of factor were used (Montgomery, 2009). In this method several factors are changed simultaneously in order to find out the most important factors and the possible interactions of the factors. The studied factors were temperature, NaOH concentration, liquid-solid ratio (cm^3/g), stirring rate and oxygen or nitrogen gas bubbling. The extreme values of factors range were chosen to be certain that the factors will have clear effect. The used temperatures were 25 and 95 °C, and concentrations of NaOH solutions were 2 and 8M. The chosen liquid-to-solid ratios (cm^3/g) were 5 and 30. A stirring rate was adjusted to 100 or 400 rpm, and more oxidative or less oxidative conditions were adjusted using oxygen or nitrogen gas bubbling.

Table 3. Factorial (2^{5-2}) test series used in the leaching experiments

N°	NaOH,M	L/S ratio	Temp., °C	Bubbling with	Agitation, rpm
1	2	5	25	O_2	400
2	8	5	25	N_2	100
3	2	30	25	N_2	400
4	8	30	25	O_2	100
5	2	5	95	O_2	100
6	8	5	95	N_2	400
7	2	30	95	N_2	100
8	8	30	95	O_2	400

The experimental setup for the leaching test consisted of a thermobath (Lauda AquaLine AL25), glass reactor and motor driver stirrer (VWR VOS16). The cover of the glass reactor provided through holes for a mercury thermometer, gas bubbling, stirrer and sampling/feeding. A water-cooled condenser was added to the structure at higher temperatures. The NaOH solutions were prepared from technical grade grains and distilled water, and a volume of 800 cm^3 was set into reactor. Oxygen or nitrogen gas was fed into the reactor for 1 hour and after that 26.67 g or 160 g of dust was charged and the stirring rate was adjusted. A liquid sample was taken off and filtered in the chosen time intervals of 5, 10, 15, 20, 25, 30, 60 and 120 minutes for EAF1 dust, and 5, 15, 30, 60 and 120 minutes for EAF2 dust. The stirring was stopped 30 seconds before each sampling. After filtering the leach samples were analysed for the

amount of leached Zn with a Perkin Elmer 372 AAS device. A part of the samples after 120 min of leaching was analyzed more precisely with a multi-element ICP-AES analysis in order to investigate which other elements leached with zinc.

Results and discussion

The main response under investigation was the percentage of zinc extraction from EAF1 and EAF2 dusts in the leach liquor. The leaching curves of zinc from the 2^{5-2} fractional factorial experiments are shown in Figs. 2 and 3. From the shape of the leaching curves it can be observed that dissolution of zinc is fast, occurring in a few minutes, and then increased only slightly. The maximum amount of leachable zinc in one experiment was usually achieved at the end of the test, which was 120 min of leaching. In a few experiments the plateau was achieved earlier, and then amount of leached zinc decreased that may indicate that part of zinc was precipitated back.

Under the present experimental conditions, zinc extraction varied from 14 to 61% for EAF1 dust. Generally, extraction was lower for EAF2 dust and varied from 8 to 33%. The difference in zinc extraction was arisen most likely from the mineralogical differences of dusts. In addition to zinc oxide, zinc ferrite was also identified in both dusts. Zinc ferrite is difficult to dissolve in alkaline solutions and zinc extraction is dependent on the amount of zinc in ferrite from.

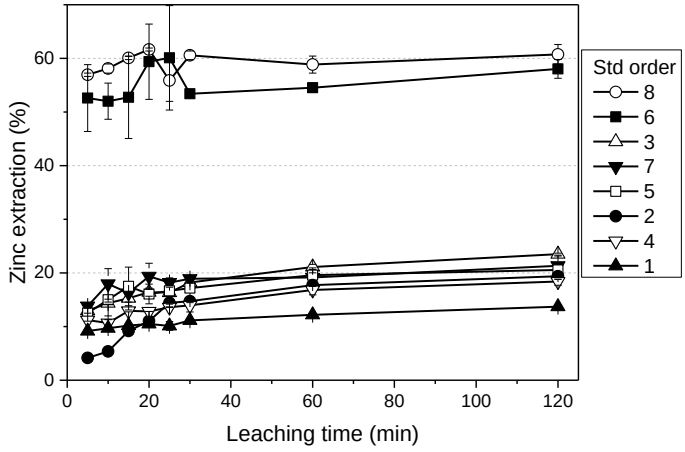

Fig. 1. Leaching curves of zinc dissolution from EAF1 dust according to results from 2^{5-2} fractional factorial design

As can be clearly seen from Figs. 1 and 2 that zinc extraction is higher under two leaching conditions. In both, strong 8 M NaOH solution with high temperature and stirring rate was used, but bubbling gas and liquid-to-solid ratio changed. Almost equivalent zinc extraction was achieved under these two leaching conditions. From

EAF1 dust around 60% of zinc and from EAF2 dust slightly over 30% of zinc was dissolved.

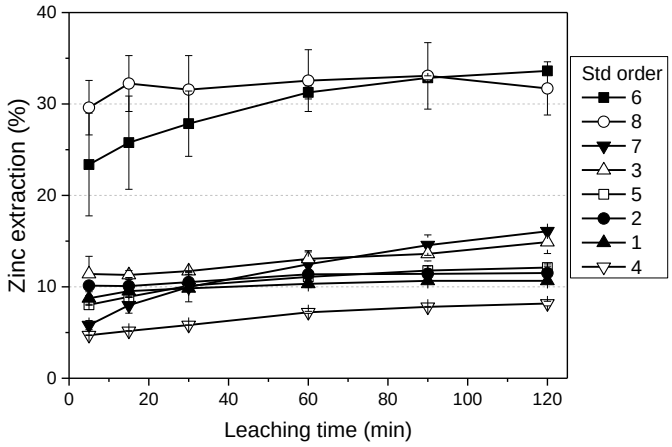

Fig. 2. Leaching curves of zinc dissolution from EAF2 dust according to results from 2^{5-2} fractional factorial design

To study the effect and possible interaction of the leaching factors on zinc dissolution, the results were analyzed using the Minitab 16 software. Figure 3 shows the pareto charts of the standardized effects of the studied factors after 120 min leaching. Mainly, the same trends can be observed for both dusts. Temperature, NaOH concentration and agitation speed were statistically strongly significant factors of zinc dissolution in both dusts. The liquid-to-solid ratio (L/S) and bubbling gas were only somewhat significant for the EAF1 dust and for the EAF2 dust the L/S ratio was even insignificant. The response was positive for all of the studied quantitative factors and

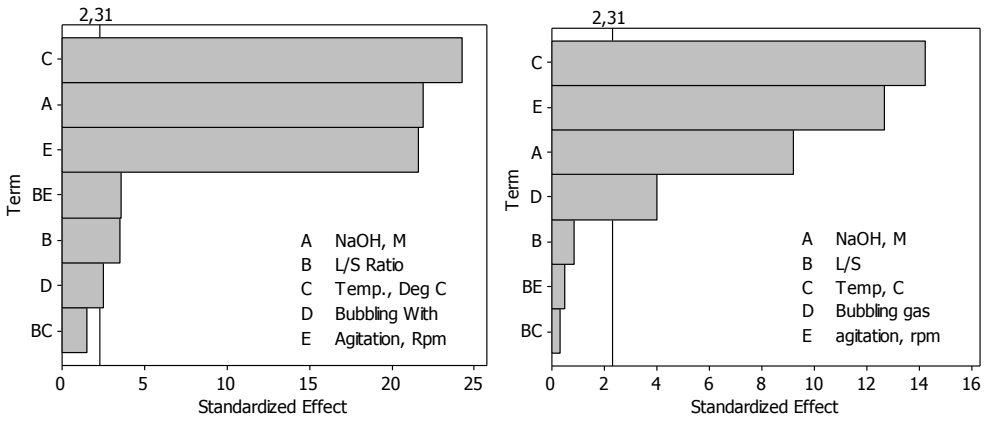

Fig. 3. Pareto chart of standardized effects of studied factors (response is Zn extraction %, alpha = 0.05) for EAF1 (left) and EAF2 (right) dusts

dissolution of zinc was enhanced with increasing level of the factors. Gas bubbling was a qualitative factor and oxygen gas bubbling had a negative response versus dissolution of zinc was enhanced with nitrogen gas bubbling.

Figures 4 and 5 show the interaction charts of the studied leaching factors (determined from extractions after 120 min leaching). The interaction between the factors occurs when the effect that one factor has on the output is dependent on the level of another factor, and the response is different at the low level of the second factor than at the high level of the second factor. For both EAF1 and EAF2 dusts two-factor interactions were found between NaOH concentration and temperature, NaOH concentration and agitation, liquid-to-solid ratio and bubbling gas, and between temperature and agitation. Three of these four interactions were between the factors that stood out with stronger effect on zinc dissolution. The interactions with NaOH

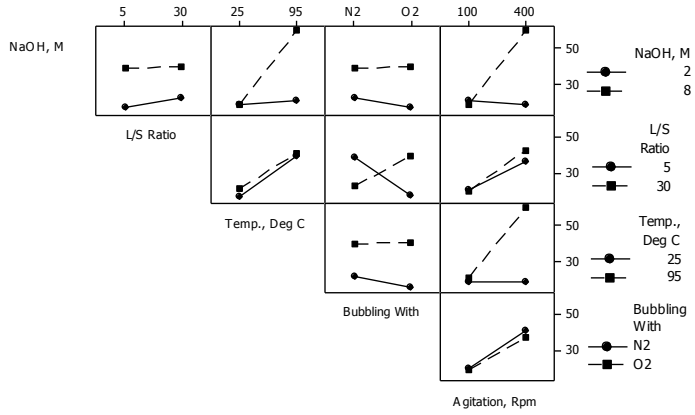

Fig. 4. Interactions of studied factors for EAF1 dust

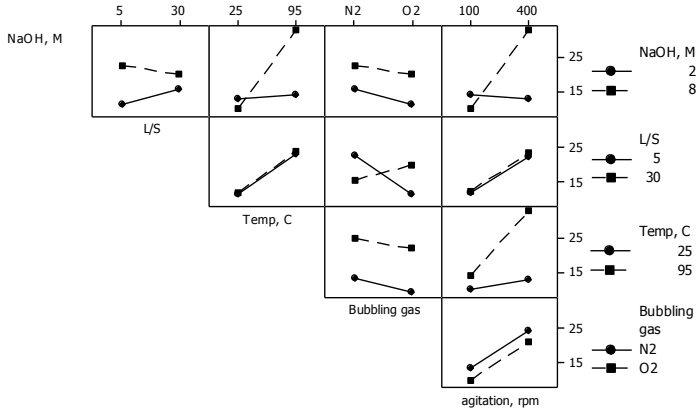

Fig. 5. Interactions of studied factors for EAF2 dust

concentration, stirring rate and temperature are explained by high viscosity of strong NaOH solution. Strong agitation and high temperature enhanced the extraction/dissolution of zinc in strong viscous NaOH solution. The reason for interaction between liquid-to-ratio and bubbling gas is unclear. Bubbling with oxygen reduced zinc extraction with high amount of solid but enhanced it when the amount of solid was low. In the EAF2 dust, the interaction between NaOH concentration and liquid-to-solid ratio was also found. Zinc extraction was slightly increased in low NaOH concentrations but slightly decreased in strong NaOH solution, when small amount of solid was used, but this interaction was not so obvious.

It should be noted that the 2^{5-2} fractional factorial design used in this leaching experiments is a resolution III design, when the main effects are confounded with two-factor interactions. The resolution describes the ability to separate the main effects and interactions from one to another. To increase the resolution and eliminate the confounding between the main effects and two-factor interactions a full fold-over design, in which the signs of all the factors are reversed, can be run and combine to the design used in this study. This would provide clearer basis for optimization of leaching conditions.

The results from the ICP-AES analyses are presented in Table 4. The results showed that zinc was leached selectively. Practically no iron (usually <1.5 mg/dm^3) and nickel (< 0.1–0.21 mg/dm^3) was dissolved. The leaching conditions had only minor effect on dissolution of chromium and less than 3% of chromium was leached from both dusts. In some samples from the EAF2 dust the amount of lead and cadmium was a bit higher, however only 9% of lead and 1% of cadmium was leached. Also the leaching recovery of molybdenum was higher for the EAF2 dust (40 – 60%). As iron and of the valuable alloying elements chromium and nickel remained in the leach residue, for recovering the valuables, the residue could be recycled back into furnaces if the amount of zinc can be lowered to a sufficient level.

Table 4. Amount of certain elements in leachate after 120 min leaching

	Amount in leachate (mg/dm^3)							
	Zn	Fe	Cr	Ni	Mo	Ca	Pb	Cd
EAF1	169 - 8690	< 1.5	43- 277	<0.1 - 0.21	4 - 32	< 5 - 7	3 - 62	< 0.25
EAF2	145 - 3234	<1.5 - 15.5	47 - 446	≤ 0.11	18.3 - 263	<5 - 14.6	<2.5 - 188	<0.25 - 6.51

Conclusions

Dusts formed in stainless steel production are considered as a harmful waste in most industrial countries. At the same time these dusts are also a source of valuable metals but their extraction and recovery is difficult due to their complex composition. The most troublesome element in the dust is zinc, which vaporizes easily and condenses into steel production fumes ending up in the flue dust or sludge, usually as oxide or ferrite. In this study two electric arc dusts (EAF1 and EAF2) from stainless steel

production were leached in NaOH solutions aiming to selectively leach out zinc from the dusts, and to find the effect of various leaching factors on dissolution of zinc/find factors that affected most on zinc dissolution.

The results from (2^{5-2}) fractional factorial tests showed that all studied factors (NaOH concentration, temperature, agitation, solid-to-liquid ratio, and oxygen/nitrogen gas bubbling) had statistically significant effect on zinc dissolution, except the solid-to-liquid ratio for the EAF2 dust. However, an increase in the NaOH concentration, temperature and agitation improved zinc extraction preferentially. Two-factor interactions were found between those three factors and also between liquid-to-solid and bubbling gas.

From all the experiments performed in this work, two of them gave higher zinc extraction. In both, strong 8 M NaOH solution with high temperature and stirring rate was used, but bubbling gas and liquid-to-solid ratio changed. Almost equivalent zinc extraction achieved under these two leaching conditions was around 60% for the EAF1 dust and over 30% for the EAF2 dust. The difference in zinc extraction between the dusts arose from the mineralogical differences and is dependent on the amount of zinc in ferrite form.

This study showed that alkaline leaching of zinc from stainless steel EAF dusts using NaOH solutions is selective and practically no iron, chromium and nickel were dissolved. However, the dissolution of zinc is limited due to the presence of zinc ferrites that remains the main problem to be solved. When considering the possibility to recycle dust back to the process, the amount of zinc should be low to effectively recycle dust back to the process. The leaching process can be used in zinc removal if zinc ferrites are decomposed prior to leaching, for example by roasting.

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